

Albumen-mediated Green Synthesis of ZnFe₂O₄ Nanoparticles and Their Physico-Chemical Properties

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Abstract: Spinel ferrites with general formula AB₂O₄ possess charming magnetic and electrical properties owing to their thermal and chemical steadfastness. Spinel zinc ferrite (ZnFe₂O₄) nanoparticles have attracted massive attention due to their unusual amalgamation of properties, especially magnetic properties, where these properties are equipped as suitable candidates in the field of electronics. Here, a simple self-combustion technique is made with the assistance of albumen to synthesize nanocrystalline zinc ferrite (ZnFe₂O₄) particles. The egg white (albumen) that is used in the synthesis process plays the fuel role in the process of combustion. The results of the powder X-ray diffraction (PXRD) and Fourier Transform Infrared Spectroscopy (FTIR) suggested that the synthesized nanoparticles are of single phase and show spinel structure. The photoluminescence studies reported a doublet peak at around 360-380 nm. The functional groups present in the synthesized nanoparticles were revealed from FTIR data. EDX findings give an account of the percentage composition of the elements Fe, Zn and O present in the synthesized sample. High-resolution Scanning Microscope (HRSEM) reveals the agglomerated coalescence nature of ferrite nanoparticles.

Keywords: Ferrite, PXRD, FTIR, HRSEM, EDX Albumen.

1. Introduction

Ferrites are of interest due to their electrical, magnetic and mechanical properties, which can be adapted to the requirements of device manufacturing and biological applications. Magnetic Nanoparticles have emerging biomedical applications in sundry areas, such as disease diagnostics, magnetic resonance imaging, sensors, actuators, magnetic storage devices, ... etc. Nano-sized ferrites of the MFe₂O₄ type are the most significant magnetic

materials which have yet to be properly investigated on the way to their physical and chemical properties. The metal-iron ratio plays a crucial role in the regulation of MFe₂O₄ nanoparticles' magnetic properties [1, 2]. Due to the increased volume fraction of surface atoms, surface effects may be crucial when reducing particle dimensions. As a competent appendage of the ferrite family, ZnFe₂O₄ has grasped researchers because of its invigorating

magnetic properties as opposed to other ferrites. After a thorough study of the solid-state reaction, this approach was adopted. It is possible to synthesize nanoparticles using physical, chemical, mechanical and thermal processes, using techniques, such as coprecipitation, sol-gel, combustion, ball milling, ... etc. But, non-toxic eco-friendly precursors, such as plant extracts and animal by-products, are used for the synthesis of nanoparticles to reduce or eliminate the use or production of toxic substances, which is known as green synthesis. The albumen-enriched egg white was first recorded by Santi Maensiri et al. [3] for the preparation of ferrites substituted for transition metal. The magnetic, electrical, optical, morphological and other properties of nanoparticles can be studied using various tools, such as X-ray diffraction, Scanning Electron Microscope, Vibrating Sample Magnetometer, Fourier Transfer Infrared Spectroscopy, ... etc.

The ultimate objective of this work is to examine the physical, chemical and morphological properties of zinc ferrite.

2. Experimental Procedure

2.1 Preparation

Zinc ferrite magnetic nanoparticles were synthesized using ferric nitrate nonahydrate and zinc nitrate hexahydrate of high chemical purity along with freshly prepared egg white. Egg white, rich in albumen protein, is recognized for its frothing and emulsifying features and it is easily soluble in water, which makes it combine with metal ions easily. Egg white also assists as binder cum gel for shaping materials. Egg white and double distilled water are mixed in 3:1 ratio to form a homogeneous solution by vigorous stirring at room temperature for one hour. $Zn(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ are taken such that corresponding zinc to ferrite composition is 1:2 mole ratio, gradually added to the homogenous egg white solution and vigorously stirred at room temperature for four hours. pH adjustments are not made during the process. Then, the mixed solution was heated on a hot plate at 80°C for several hours until a dried precursor was obtained. Then, the synthesized

powder was calcined in a muffle furnace at 600°C for 3 hours [4].

2.2 Characterization

The calcined zinc ferrite nanoparticles were characterized using X-ray diffractometer, Fourier Transform Infrared spectroscopic analysis using KBr pellets, High-resolution Scanning Electron Microscopy and Energy Dispersive X-ray spectroscopy analysis. The crystallite phase of the zinc ferrite was confirmed by X-ray diffraction using XPERT PRO diffractometer. The infrared analysis of the Fourier Transform was reported using the IFS66V FT-IR spectrometer from Bruker. The morphology of the prepared samples was studied using High-resolution Scanning Electron Microscopy.

3. Results and Discussion

3.1 X-ray Diffraction Analysis

The PXRD profile of $ZnFe_2O_4$ nanoparticles is illustrated in Fig. 1. The typical reflection at (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) in the figure corresponds to face-centered cubic spinel structure of $ZnFe_2O_4$ matching incredibly well with the JCPDS card No.22-1012. The lattice parameter of the prepared zinc ferrite nanoparticles is found to be $a = 8.4056 \pm 0.01 \text{ \AA}$ from UNITCELL software. The particle size of $ZnFe_2O_4$ is calculated using Debye-Scherrer formula and it was found to be ranging from 30 to 62 nm. X-ray density and hopping length of $ZnFe_2O_4$ nanoparticles were obtained as $\rho_x = 5.3706 \text{ g/cc}$, $d_A = 3.639 \text{ \AA}$ and $d_B = 2.9718 \text{ \AA}$, respectively.

The X-ray density (ρ_x) is calculated using the following formula (Eq. 1):

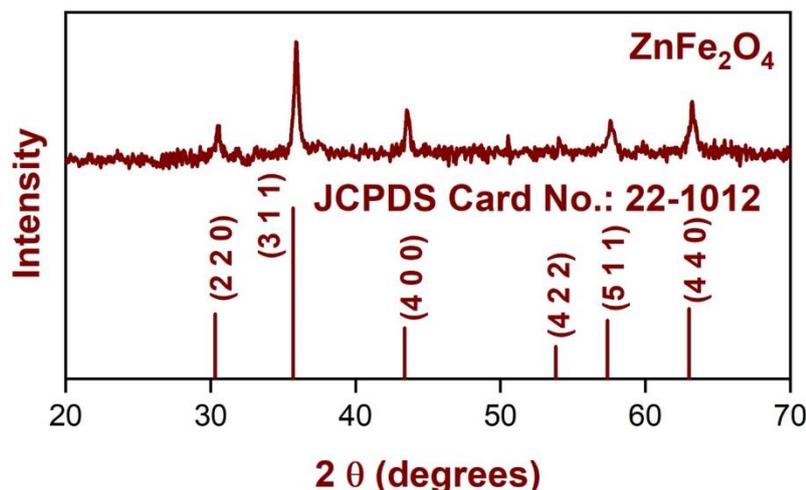
$$\rho_x = \frac{8M}{Na^3} \quad (1)$$

where M, N and a represent molecular weight, Avogadro number and lattice constant of the nanoparticles [4, 5].

And Eqs. 2 and 3 are used to calculate the values of the hopping lengths of the tetrahedral (A) and octahedral (B) sites [6].

$$d_A = 0.25a\sqrt{3} \quad (2)$$

$$d_B = 0.25a\sqrt{2} \quad (3)$$


 FIG. 1. XRD pattern of ZnFe₂O₄.

3.2 Fourier Transform Infrared Analysis (FT-IR) Measurement

FTIR confirms the formation of spinel structure in ZnFe₂O₄. FTIR spectra of the prepared zinc ferrite samples were recorded in the wave number range of 4000 to 400 cm⁻¹ and portrayed in Fig. 2. Two main broad metal – oxygen bands are seen in the samples, with the higher one (ν_1) in 546 cm⁻¹ is caused by the stretching vibrations of the tetrahedral metal – oxygen [Fe–O] band, while the lower one (ν_2) in the range 432 cm⁻¹ is caused by the metal – oxygen [Zn – O] vibrations in the octahedral sites. The values of force constant are calculated for ZnFe₂O₄ as 2.1808 Nm⁻¹ and 1.365 Nm⁻¹, respectively.

The values of the force constants K_T and K_O for corresponding frequencies ν_1 and ν_2 of the

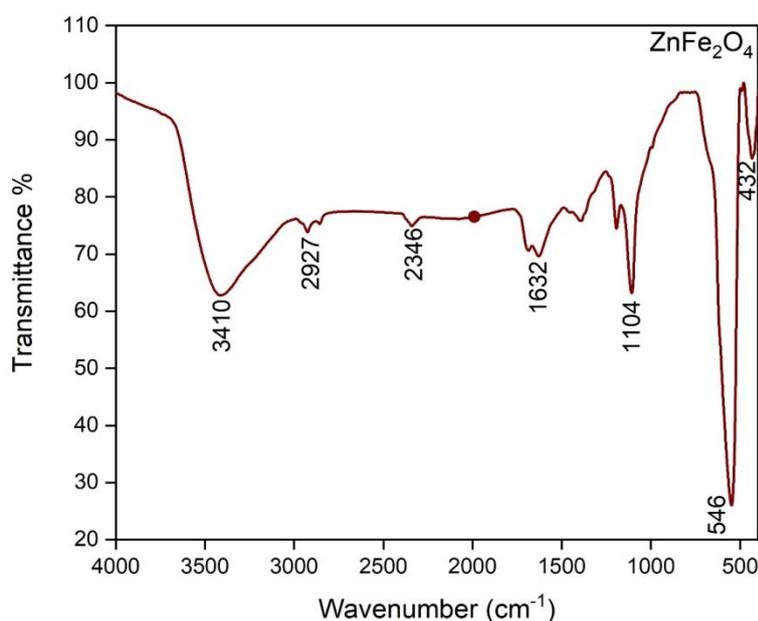
A- and B-sites of ZnFe₂O₄ are calculated using the formulae given below [7].

$$K_T = 4\pi c^2 \nu_1^2 \mu \quad (4)$$

$$K_O = 4\pi c^2 \nu_2^2 \mu \quad (5)$$

where, c is the velocity of light, ν_1 and ν_2 are the frequency of vibration of the A- and B-sites and μ is the reduced mass for the Fe³⁺ ions and the O²⁻ ions, which is approximately equivalent to 2.065x10⁻²³g.

The bands observed around 3410 and 1632 cm⁻¹ are attributed to the tensional stretching modes of water molecules absorbed by the nanoparticle. The stretching vibration of the carboxylate group (CO₂²⁻) is witnessed at 2927 cm⁻¹ and 2346 cm⁻¹. The band at 1104 cm⁻¹ links to nitrate ion traces [3, 4, 8-10].


 FIG. 2. FTIR pattern of ZnFe₂O₄.

3.3 EDX and HR-SEM Analysis

The elements present in the zinc ferrite nanoparticles are surveyed using EDX spectra. The EDX spectra of ZnFe_2O_4 are depicted in Fig 3. The peaks at around 0.7 eV, 6.4 eV and 7 eV in the spectra approve the existence of iron in the Zinc Ferrite nanoparticles. The peak at around 0.5 eV in the spectra reveals the existence of oxygen. The peaks at 1.1 eV, 8.7 eV and 9.6 eV in Fig. 3 relate to the existence of zinc [11].

The morphology of the synthesized zinc Ferrite nanoparticles is recorded using HR-SEM. The HR-SEM image of ZnFe_2O_4 at the magnification of 500 nm is portrayed in Fig. 4. From the figure, it is evident that the particle

size of ZnFe_2O_4 varies from 15 to 55 nm. There is a considerable degree of accumulation of uniform spherically formed zinc ferrite nanoparticles. The agglomeration arises in ferrite nanoparticles owing to their magnetic nature and the binding of primary particles held together by fragile surface interactions, such as Vander Waals force [12]. From Gaussian fit in Fig. 4, the maximum and minimum diameters of the ZnFe_2O_4 nanoparticles have been determined and the values are found to be 51.43 and 16.97 nm, respectively. The standard deviation of zinc ferrite nanoparticles was found to be 7.138 nm [13]. The particle size agrees well with the particle size calculated from XRD data.

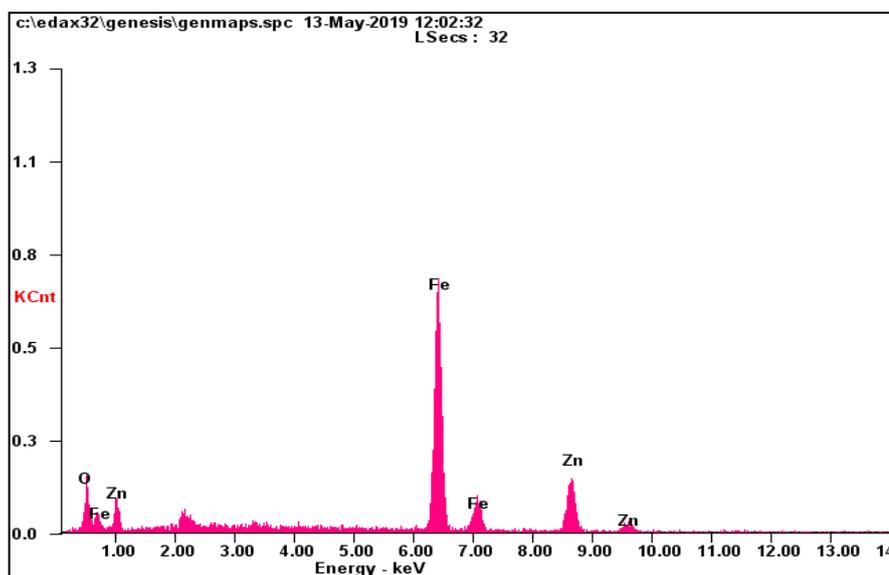


FIG. 3. EDX spectra of ZnFe_2O_4 .

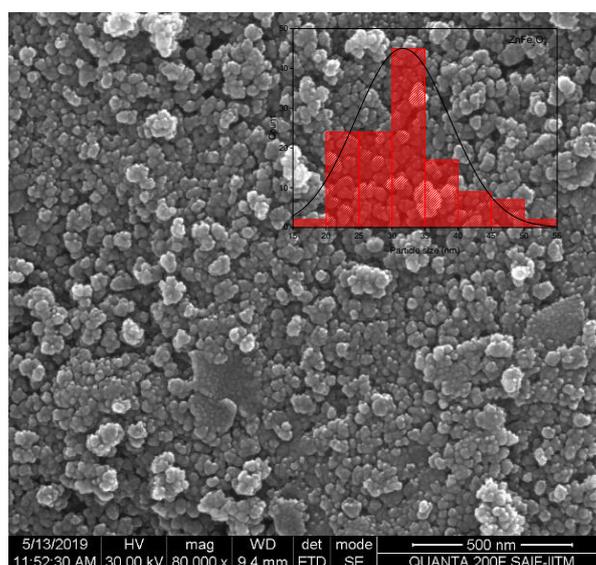


FIG. 4. Particle size distribution of ZnFe_2O_4 .

4. Conclusion

ZnFe₂O₄ nanoparticles have been successfully prepared via simple self-combustion method using albumen (a protein in egg white) as fuel. The gel formed by water soluble egg white has served as a matrix for the entrapment of metal ions. From the XRD analysis, it is found that ZnFe₂O₄ exhibits a cubic spinel structure with particle size varying

from 30 to 62 nm. FTIR spectra confirmed the spinel structure from the two main broad metal-oxygen bands in the spectra. From HR-SEM analysis, the prepared zinc ferrite nanoparticles were found to be accumulated uniform spherical particles. EDX spectra show the presence of Zn, Fe and O in the ZnFe₂O₄ nanoparticles.

References

- [1] Vinosha, P.A., Mely, L.A., Jeronsia, J.E., Monica, F.H., Raja, K. and Das, S.J., *Nano Hybrids and Composites*, 17 (2017) 1.
- [2] Sundararajan, M., Sailaja, V., Kennedy, L.J. and Vijaya, J.J., *Ceramics International*, 43 (2017) 540.
- [3] Maensiri, S., Masingboon, C., Boonchom, B. and Seraphin, S., *Scripta Materialia*, 56 (2007) 797.
- [4] Udhaya, P.A., Bessy, T.C. and Meena, M., *Materials Today: Proceedings*, 8 (2019) 169.
- [5] Vinosha, P.A., Mely, L.A., Jeronsia, J.E., Krishnan, S. and Das, S.J., *Optik*, 134 (2017) 99.
- [6] Nikam, D.S., Jadhav, S.V., Khot, V.M., Bohara, R.A., Hong, C.K., Mali, S.S. and Pawar, S.H., *RSC Advances*, 5 (2015) 2338.
- [7] Vijaya Babu, K., Satyanarayana, G., Sailaja, B., Santosh Kumar, G.V., Jalaiah, K. and Ravi, M., *Results in Physics*, 9 (2018) 55.
- [8] Udhaya, P.A., Meena, M. and Queen, M.A.J., *International Journal of Scientific Research in Physics and Applied Sciences*, 7 (2019) 71.
- [9] Sundararajan, M., Kennedy, L.J., Aruldoss, U., Pasha, S.K., Vijaya, J.J. and Dunn, S., *Materials Science in Semiconductor Processing*, 20 (2015) 1.
- [10] Udhaya, P.A. and Meena, M., *Materials Today: Proceedings*, 9 (2019) 528.
- [11] Li, L., Bi, H., Gai, S., He, F., Gao, P., Dai, Y., Zhang, X., Yang, D., Zhang, M. and Yang, P., *Scientific Reports*, 7 (2017) 43116.
- [12] Babić-Stojić, B., Jokanović, V., Milivojević, D., Jagličić, Z., Makovec, D., Jović, N. and Marinović-Cincović, M., *Journal of Nanomaterials*, 2013 (2013) 741036.
- [13] Jeseentharani, V., George, M., Jeyaraj, B., Dayalan, A. and Nagaraja, K.S., *Journal of Experimental Nanoscience*, 8 (3) (2013) 358.