Düzce University
Journal of Science & Technology

Research Article

Synthesis, Dielectric and Magnetic Characterization and Properties of Nano Magnetic Particles by using Microwave Technique

Harun BAYRAKDAR [a,*]

[a] *Department of Mechanical Engineering, Faculty of Engineering, Düzce University, Düzce, TÜRKİYE*
** Corresponding author's e-mail address: harunbayrakdar@duzce.edu.tr*
DOI: 10.29130/dubited.1647176

ABSTRACT

A microwave-induced combustion method has been utilized to prepare nano-sized powders of hexagonal ferrites using urea and glycine as fuel. The dielectric and magnetic properties of these products were investigated experimentally, the dielectric properties were investigated with the RF LCR device, the magnetic properties were investigated with the Electron Spin Resonance (ESR) and Vibration Sample Magnetometer (VSM) spectrometer, and the crystalline structure was investigated with the X-ray diffraction (XRD) device.

Keywords: *Nanoparticles, Hexagonal ferrites, Dielectric behavior, Magnetic behavior, Polarization*

Mikrodalga Tekniğini Kullanarak Nano Manyetik Parçacıkların Sentezi, Dielektrik ve Manyetik Karakterizasyonu ve Özellikleri

ÖZ

Nano boyutta hekzagonal ferritlerin hazırlanması için üre ve glisin yakıt olarak kullanarak, mikrodalga kaynaklı yanma yöntemi kullanılmıştır. Bu ürünlerin dielektrik ve manyetik özellikleri deneysel olarak incelendi, dielektrik özellikleri RF LCR cihazı ile incelendi, manyetik özellikleri Elektron Spin Rezonans (ESR) ve Titreşim Numune Manyetometresi (VSM) spektrometresi ile incelendi ve kristalin yapısı X-ışını kırınımı (XRD) cihazı ile incelendi.

Anahtar Kelimeler: *Nanopartiküller, Hekzagonal ferritler, Dielektrik davranış, Manyetik davranış, Polarizasyon*

Received: 26/02/2025, Revised: 18/03/2025, Accepted: 07/04/2025

I. INTRODUCTION

As the needs of human beings change and develop, today's technologies change and develop in parallel with them. Unhealthy diet, developments in communication ways, wireless communications, developments in the defense industry, etc.. It has become a threat to us as if it was an invitation to diseases in human beings [1], biomedical applications [2], ferrites exhibit soft magnetic behavior due to their structural properties and are used in different applications such as contrast agents in MRI, magnetic fluids, drug delivery and gas sensors [3-7], Biocompatible nanosized magnetic particles (MNPs) based on iron oxide NPs are essential components for biomedical applications such as drug delivery systems [8-10], hyperthermia [11]. Magnetic recording systems and quantum processors can be made at room temperature [12].

There are three main categories of synthesizing magnetic NPs: biological, physical, and chemical methods [1]. In this study, we demonstrate the synthesis of hexagonal ferrite nanoparticles (NPs) by a microwave-assisted combustion method by using glycine and urea. They remove the water molecules in the cellulose before they reach the ignition temperature and prevent further combustion by covering the surface of the coal formed.

In this study, the dielectric and magnetic behavior of hexagonal ferrite nanoparticles (NPs) were studied using a LCR Meter for dielectric measurements and magnetic behaviors were measured using Electron Spin Resonance (ESR) and Vibrating Sample Magnetometer (VSM) spectrometers. Synthesized nano-crystalline samples were structure characterized by x-ray diffraction (XRD).

II. SYNTHESIS OF NANOPARTICLES

Nanoparticles of hexagonal ferrite were prepared by microwave-induced combustion with glycine (NH_2CH_2COOH) and urea ($CO(NH_2)_2$). These nanoparticles were prepared using the method described in refs [14] with some modifications. Sodium dodecyl sulfate (SDS), glycine and urea to be used as fuel were dissolved in deionized water and poured into a crucible, then placed in a microwave oven [15].

In the microwave process; with the interaction of microwaves with the material, heat is produced in the sample itself; this heat pushes the water and moisture in the samples, resulting in a more desired sample [14]. In this study, glycine and urea were used as the precipitating/reducing agent to prevent local precipitation and thus to provide a homogeneous shape that provides a wide particle size distribution.

III. EXPERIMENTAL

X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance diffractometer with Cu Kα radiation.

For dielectric measurements, an Agilent 4287A RF LCR Meter was used in the frequency range of 1 MHz-3 GHz at room temperature. Both surfaces of the samples were coated with Ag-epoxy. In dielectric measurements, the cross-sectional area (A) and the stack thickness (distance between contacts) (d) were measured.

Quantum Design Vibrating Sample Magnetometer (VSM) Model 6000 was used for magnetic measurements. X-band (f≈9.7 GHz) Bruker EMX model spectrometer was used for ESR measurements.

IV. RESULTS AND DISCUSSION

A. XRD MEASUREMENTS

XRD results are shown in Figures 1. The pattern exhibits the diffraction peaks of powders which correspond to (110), (1013), (116), (119), (024), (300), (2113), (1025), and (220). The measurement results show that NPs. are the y type hexa-ferrite structure [15]. As seen from the XRD measurement results of the nanoparticles, the highest peak (1013) proves that these samples are Y-type hexagonal ferrite and was calculated by ref 12,15. The lattice parameters (a and c) and unit cell volume (V) for the single phase sample were calculated by the following formulas, respectively [12]; $\mathrm{Sin}^2\theta=\lambda/3a^2 (h^2+hk+k^2) + \lambda^2/4c^2 (l^2)$ and $V= a^2c \sin 120^0$ where "hkl" are the Miller indices, l is the wavelength, a and c are the lattice parameters. The observed values of the lattice parameters (a= 7.76 Å, c = 38.85 Å) and unit cell volume (1287.57 $Å^3$) very close to the values stated for Y-type hexagonal ferrites [12,15]. With the Debye-Scherrer equations used for XRD measurements;

$$D=(0.9\lambda)/(B\cos\theta_B) \qquad (1)$$

where λ, B and θ_B are the wavelength of the X-ray source and the full width at half maximum (FWHM) and the angle of Bragg diffraction. For XRD, the intensity is

$$D_{Xray} = \frac{8M}{Na^3} \qquad (2)$$

where M is molecular weight of the sample, N is Avogadro's number, and a^3 is volume of unit cell [12].

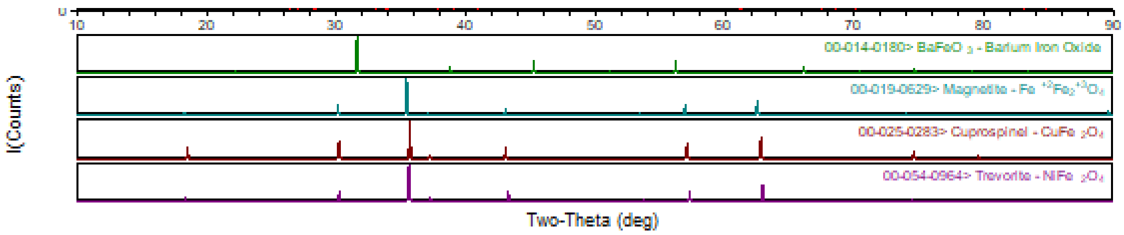


Figure 1. *XRD results*

B. DIELECTRIC MEASUREMENTS

B.1. Theory

In general, dielectric mechanisms are divided into relaxation and resonance processes. The most common are [16-18] electronic polarization, atomic polarization, dipole relaxation, and ionic relaxation. A theoretical study was conducted in ref [16,18].

From Clausius–Masotti equation,

$$\frac{\varepsilon' - 1}{\varepsilon'' + 2} = \frac{4\pi}{3} N\alpha$$

$$\alpha = \frac{e^2(w_0^2 - w^2 + iw\gamma)}{m[(w_0^2 \pm w^2)^2 + \gamma^2 w^2)]} = \frac{e^2(w_0^2 - w^2)}{m[(w_0^2 \pm w^2)^2 + \gamma^2 w^2)]}$$

$$+ i\frac{e^2 w\gamma}{m[(w_0^2 \pm w^2)^2 + \gamma^2 w^2)]}$$

$$\varepsilon' = 1 - \frac{(4\pi e^2 N/m)(w_1^2 - w^2)}{(w_1^2 - w^2)^2 + \gamma^2 w^2}$$

$$\varepsilon'' = \frac{(4\pi e^2 N/m)\gamma w}{(w_1^2 - w^2)^2 + \gamma^2 w^2};$$

As can be seen, resonance phenomena can be observed in every frequency region. This is also consistent with the experimental results.

B.2. Dielectric Measurements Results

As we know the dielectric permittivity is, $\varepsilon = \varepsilon' - i\varepsilon''$, where ε' is the reel part and ε'' is the imaginary part of the dielectric constant. As seen in Figure 2, it is clear that nanopowders in various compositions show almost the same trend and also both ε' and ε'' are sensitive to metallic behavior. The urea and glycine exhibits that the values of the real part of the ε' of complex permittivity increase with increasing frequency, with the exception of a resonance peak around 2.2 GHz [16].

The increase in both imaginary and real parts as the frequency increases and the transition to resonance is related to the high conductivity of the hexagonal ferrites of the samples. While it is stated in the literature that resonance can occur in the very high terrestrial voltage region, as can be seen from my previous publication, it has been proven both theoretically and experimentally that this resonance formation can occur in every region [16]. The resonance event is caused by atomic and electronic polarization.

In general, the resonance phenomenon, which is said to originate from vacancies or pores, is dominant in the low-frequency regions as long as the materials contain space charges. High-frequency resonances are attributed to the atomic and electronic polarizations mentioned earlier [16].

Therefore, the resonance phenomenon observed in the curves of both real and imaginary parts of the complex permittivity can be interpreted as different compositions of hexagonal ferrites using urea or glycine, which has an intrinsic property for the atomic polarization of the samples we synthesized [16].

a) b)

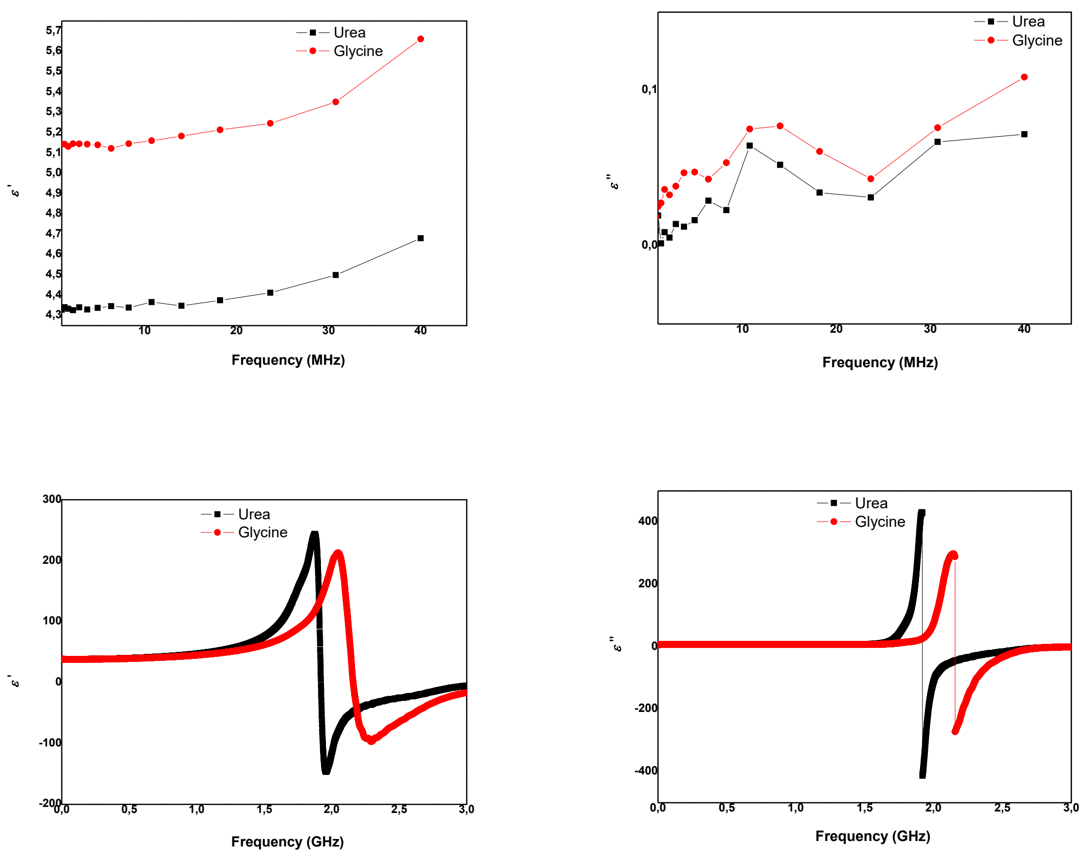


__Figure 2.__ Dependency of real and imaginary part of permittivity on frequency for __(a)__ and __(b)__.

B. 3. Magnetic Measurements

a) **b)**

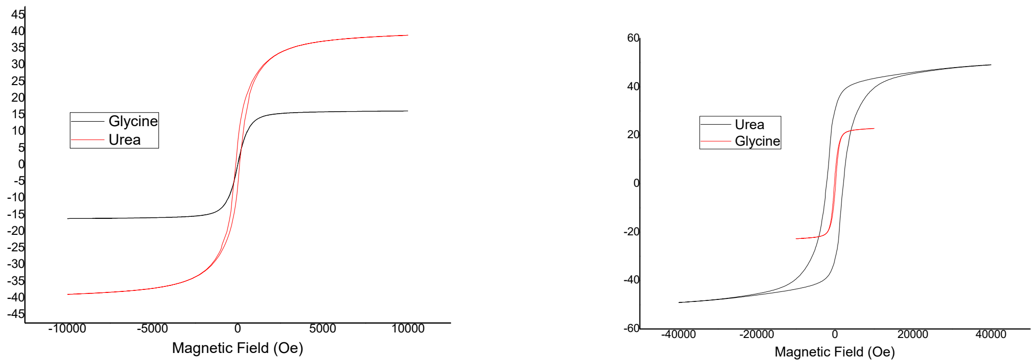


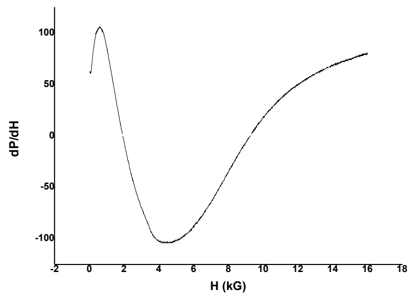
__Figure 3.__ VSM measurements __a)__ at room temperature __b)__ 10 K temperature

Magnetization measurements of hexagonal ferrite nanoparticles were carried out using the VSM technique, and the results of the M-H curves of the sample are shown in Figure 3a) at room temperature and b) at 10 K temperature.

The coercivity (H_c) of magnetic materials is generally due to magneto-crystal anisotropy. We can see from the measurement results that the magnetic moment value of urea used for synthesis is higher than glycine. According to these results, we can say that the anisotropic properties of hexagonal ferrites produced with urea are higher than those produced with glycine. As can be seen, you can see that there is a typical super paramagnetic hysteresis loop shape.

It can be said that the reason for the increase in coercivity at low temperature is the exchange anisotropy. In magnetic materials, the coercive field increases as the temperature is lowered. It has the highest value at the lowest temperature. It can be seen that the coercivity and magnetization of hexagonal ferrites increase with decreasing temperature. In addition, coercivity and magnetization increase with increasing urea.

The asymmetric behavior of nano-sized hexagonal ferrites is shown in Figure 4. These measurements are associated with superparamagnetic behavior. Additionally, ESR spectrometer measurements of hexagonal ferrites were oriented from the magnetization field relative to the freezing field [12,17].



Figures 4. *ESR spectrometer measurements*

The very broad ESR spectra of NPs, that is, the asymmetric properties they exhibit, are due to the dipolar interactions between ions and hard magnetic materials [12].

ESR spectrometer measurements have been explained in detail in our previous studies [12,17]. As can be seen from the measurement results, a very successful study has been carried out. It has very useful results scientifically. There are very useful and useful results for biomedical and cancer applications used recently from ESR measurements [1,18].

We can say that these samples we synthesized can also be used quite successfully in magnetic recording, electromagnetic absorption, and electromagnetic interference suppression applications.

V. CONCLUSIONS

It can be seen that microwave method is very useful for powder technology. It has been shown that hexagonal ferrite nanoparticles obtained using this method can be obtained in a much faster, more reliable, cheaper and crystalline structure in nano size. The dielectric behavior of the NPs was studied at room temperature. Dielectric measurements showed that the complex permittivity of composites was significantly modified by the incorporation of nanoparticles with different hexagonal ferrites ratios. Dielectric measurements produce very interesting results. The resonance phenomenon occurring in both the real and imaginary parts of the complex permittivity can be interpreted as atomic polarization.

Magnetic measurements have shown that the coercivity of hexagonal ferrite nanoparticles increases at low temperatures and with the amount of urea used. We can say that the higher coercivity at low temperatures is due to the exchange anisotropy resulting from the spin disorder of the particles. This method provides a rapid and reproducible route for the preparation of hexagonal ferrite using urea as fuel and offers a new route for the synthesis of similar magnetic materials.

These products can be used in magnetic recording media, electromagnetic absorbtion materials, radiofrequency coil manufacturing, transformer cores, biosensors, microwave devices, industrial and medical applications.

VI. REFERENCES

[1] S.R. Mokhosi, W. Mdlalose, A. Nhlapo and M. Singh, "Advances in the synthesis and application of magnetic ferrite nanoparticles for cancer therapy", *Pharmaceutics*, vol. 14, pp. 937, 2022.

[2] M. Irfan, N. Dogan, A. Bingolbali, F. Aliew, "Synthesis and characterization of $NiFe_2O_4$ magnetic nanoparticles with different coating materials for magnetic particle imaging (MPI)" *Journal of Magnetism and Magnetic Materials*, vol. 537, no. 1, pp. 168150, 2021.

[3] C. Xiangfeng, J. Dongli, Z. Chenmou, "The preparation and gas-sensing properties of $NiFe_2O_4$ nanocubes and nanorods", *Sens. Actuators, B*, vol. 123 (2), pp. 793-797, 2007.

[4] S. Rana, R.S. Srivastava, M.M. Sorensson, R.D.K. Verse, "Synthesis and characterization of nanoparticles with magnetic core and photocatalytic shell: Anatase TiO_2-$NiFe_2O_4$ system", *Mater. sci. Eng., B*, vol. 119 (2), pp. 144-151, 2005.

[5] Raikher, V.I. Stepanov, J. Depeyrot, M.H. Sousa, F.A. Tourinho, E. Hasmonay, R. Perzynski, "Dynamic optical probing of the magnetic anisotropy of nickel-ferrite nanoparticles", *J. Appl. Phys.*, vol. 96 (9), pp. 5226-5233, 2004.

[6] C.H. Cunningham, T. Arai, P. C. Yang, M.V. McConnell, J.M. Pauly, S.M. Conolly, "Positive contrast magnetic resonance imaging of cells labeled with magnetic nanoparticles", *Magn. reson. Med.*, vol. 53 (5), pp. 999-1005, 2005.

[7] T.-J. Yoon, J.S. Kim, B.G. Kim, K.N. Yu, M.-H. Cho, J.-K. lee, "Multifunctional nanoparticles possessing a “magnetic motor effect” for drug or gene delivery", *Angew. chem. (International ed.)*, vol. 44 (7), pp. 1068-1071, 2005.

[8] J. Dobson, "Magnetic nanoparticles for drug delivery", *Drug Dev. Res.*, vol. 67, pp. 55-60, 2006.

[9] C. Sun, J.S.H. Lee, M. Zhang, "Magnetic nanoparticles in mr imaging and drug delivery", *Adv. Drug Deliv. Rev.*, vol. 60, pp. 1252-1265, 2008.

[10] O. Veiseh, J.W. Gunn, M. Zhang, "Design and fabrication of magnetic nanoparticles for targeted drug delivery and imaging", *Adv. Drug Deliv. Rev.*, vol. 62, pp. 284-304, 2010.

[11] A. Jordan, P. Wust, H. Fahling, W. John, A. Hinz, R. Felix, "Inductive heating of ferrimagnetic particles and magnetic fluids: physical evaluation of their potential for hyperthermia", *Int. J. Hyperth.*, vol. 9, pp. 51-68, 1993.

[12] H. Bayrakdar, O. Yalçın, S. Özüm, U. Cengiz, "Synthesis and investigation of small g-values for smart spinel ferrite", *Journal of Alloys and Compounds*, vol. 869, pp. 159334, 2021.

[13] N. Kasapoglu, A. Baykal, Y. Koseoglu and M.S. Toprak, “Microwave-assisted combustion synthesis of $CoFe_2O4$ with urea, and its magnetic characterization”, *Scripta Materialia*, vol. 57, pp. 441–444, 2007.

[14] Harun Bayrakdar, “Microwave-Assisted hydrothermal synthesis of nanosheet layered hexagonal spinel ferrites for efficient electromagnetic wave absorbing”, *Langmuir*, vol. 40, pp. 13716−13720, 2024.

[15] Harun Bayrakdar, "Fabrication, magnetic and microwave absorbing properties of $Ba_2Co_2Cr_2Fe_{12}O_{22}$ hexagonal ferrites", *Journal of Alloys and Compounds*, vol. 674, pp. 185e188, 2016.

[16] Harun Bayrakdar and Kadir Esmer, “Dielectric characterization of $Ni_xCo_{1-x}Fe_2O_4$ nanocrystals thin film over a broad frequency range 1 MHz–3 GHz”, *J Appl Phys.*, vol. 107, pp. 044102, 2010.

[17] H. Bayrakdar, O. Yalçın, U. Cengiz, S. Özüm, E. Anigi, O. Topel, “Comparison effects and electron spin resonance studies of a-Fe_2O_4 spinel type ferrite nanoparticles”, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 132, pp. 160–164, 2014.

[18] Priyank Purohit, Akanksha Bhatt, Shashank Kailkhura, Bibekananda Sarkar, Samir Kumar, Gaurav Joshi, “Biomedical applications of spinel ferrite nanoparticles”, https://www.researchgate.net/publication/374534261