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Synthesis and characterization of superparamagnetic zinc-manganese ferrite nanoparticles using hydrothermal-sonochemical method for medical applications

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Abstract

In this research, zinc-manganese ferrite ZnMnFe2O4 nanoparticles with superparamagnetic properties have been synthesized by hydrothermal-sonochemical method. The contamination of spinel structures by magnetic ions, which is done in order to increase the magnetic properties of nanoparticles, is always associated with the challenge of controlling the size, shape and distribution of nanoparticles. For this reason, the choice of synthesis method becomes very important. In this research, in order to obtain nanoparticles with suitable particle distribution and magnetic properties, spinel iron oxide was doped with zinc and manganese atoms by a combination of hydrothermal and sonochemical methods. The microstructural properties of the spinel structure were investigated using X-ray diffraction, the morphological properties using a scanning electron microscope, and the magnetic properties using a vibrating sample magnetometer.

The obtained ZnMnFe2O4 nanoparticles were well distributed and showed excellent magnetic properties. The saturation magnetization of these nanoparticles was 66.5 emu/g and its incidence field was less than Oe 8. Therefore, these nanoparticles are expected to have promising applications in fields such as biomedicine and magnetic memories.

Furthermore, we hope that this new approach can pave the way for the synthesis of other inorganic nanomaterials with good monodispersity.

Key words: superparamagnetism, hydrothermal-sonochemical method, spinel structure, zinc-manganese ferrite

Introduction

In recent years, magnetic materials have become one of the most attractive research fields and research centres for technology. One of the research fields in magnetic materials is spinelliferrite nanoparticles. M.T. Farida et al., 2015). Zn-Mn ferrite as a soft magnetic material (Chandra et al., 2014) is an important part of spinel ferrite with high magnetic permeability, high magnetic saturation, and high resistance. X. (Li, R. Sun, 2015) This material has many applications in transformers, electromagnetic devices, information storage devices, sensors, radars, and microwave absorbers (Chandra et al., 2014).Controlled substitution of one or more cations in the ferrite network can affect many of their physical and chemical properties, including resistance (conductivity), optical properties (reflectance), band gap energy, and the energy and behaviour of valence and conduction bands [9]. For example, ferrite-based photocatalysts with changes in their physical and chemical properties are used for environmental purposes (water and air pollution) and solar cells.Superparamagnetic iron oxide particles can be used in various nanostructures to produce biological devices, including drug delivery systems and magnetic resonance imaging. Materials containing superparamagnetic iron oxide nanoparticles can be guided to a desired location by external magnetic fields. The biocompatibility and stability of superparamagnetic iron oxide nanoparticles can be increased by their type of coating.

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Increasing the accumulation of drugs at their site of action enables multifunctional production for simultaneous drug delivery and imaging. However, the ferrite size of magnetic nanoparticles in drug delivery has an important role in determining the amount of cellular absorption (Chandra et al., 2014) because the size effect of nanomaterials is very important in cellular absorption. Nanoparticles with a size between 10 and 100) nm are the ideal range for drug delivery. The use of magnetic nanoparticles with a size less than 2 nm is not recommended for medical use. Because nanoparticles in this range have the ability to penetrate the cell membrane and cause damage (Chandra et al., 2014), In this size range, nanoparticles have toxic effects and endanger human life. Therefore, particle size control is very important in drug delivery.Ferrite composites with different particle sizes, shapes, and distributions can be synthesised in several ways. Also, these methods are different in terms of their behaviour towards the environment [121]. Some methods, such as co-precipitation, are relatively suitable for dissolving salts because they use deionized water, while other methods use various toxic organic solvents. In the meantime, the co-precipitation method in the synthesis of spinel ferrite nanoparticles is very useful, cost-effective, suitable for large-scale production, but time-consuming, and often a usable method for synthesising nanoparticles of comparable size [129]. In this method, the liquid solution is the heart of the reaction, in which divalent and trivalent metal salts are mixed together in a 1:2 molar ratio with vigorous and continuous stirring in the basic environment. In the co-precipitation method, by changing the iron salts and ionic iron ratio, temperature, pH, and type of base used, one can change the magnetic phase and particle size. The pH is usually controlled in the solution using ammonium solution or sodium hydroxide solution.

The hydrothermal method is also widely used to produce this class of nanoparticles. This method is based on heating reactants, mostly metal salts of oxide, hydroxide, or metal powder, as a solution or suspension in a liquid (usually not necessarily water) at a high temperature and pressure of about 100 psi. The nucleation and growth of particles occur under these conditions, which create nano-oxides, metals, or non-oxide particles with controlled shape and size. In this method, nano- or micron-scale particle powders, including carbon nanotubes and colloidal quantum dots, are directly produced. The advantage of the thermal decomposition method for making magnetic nanoparticles is the size and, of course, the very precise control over the dimensions of the nanoparticles. In this method, non-polar organic compounds are used in organic solvents with a high boiling point and containing stabilising surfactants. Homogeneous nanoparticles with a very small size distribution can be easily obtained by controlling the proportions of non-polar organic materials. Initiating reagents include organometallic compounds, surfactants, and solvent reactions. By using test parameters such as temperature, heating time, and heating rate, the distribution, size, shape, and magnetic properties of nanoparticles can be controlled. [7] With the passage of time, a large number of nuclei are formed with the formation of molecular clusters in a controlled manner by the decomposition of the precursors, which is due to the characteristic of nucleation. As the temperature increases, the reaction mixture reaches the growth temperature, which leads to a homogeneous size distribution. Also, in the sonochemical method, the chemical reaction is carried out by applying ultrasonic waves, as a result of which the cavitation process and bubbles are combined in the reaction environment. The size of the particles depends on the concentration of the reactants. In this method, holes are created by passing sound waves with a constant frequency through the solution. By increasing or decreasing the power of the applied wave, the bubbles are formed and eventually disintegrate, leading to the formation of nanoparticles [11]. The advantages of this method are simplicity, the

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ability to perform at ambient temperature, the possibility of synthesising amorphous nanoparticles, the ability to introduce high-purity nanoparticles into porous materials, the ability to settle nanoparticles on the surface of ceramics and polymers, and the product being free from contamination. Disadvantages include particles sticking to each other, a very low concentration of prepared nanoparticles, carrying out the process in a protective environment, and the toxicity of consumables. The sol-gel method is also used to produce ceramic particles and homogeneous metal oxide with high purity. Although the history of ceramic production processes using chemical methods goes back centuries, the concept of controlling the shape and molecular structure of ceramics and glasses can be done using this method.In this research, superparamagnetic spinel iron oxide nanoparticles with manganese impurities were doped and synthesised. In the synthesis of these nanoparticles, iron, manganese, and zinc nitrates were used, and a combination of hydrothermal and sonochemical methods were used. The structural, morphological, and magnetic properties of nanoparticles were characterised, and the results showed the synthesis of superparamagnetic nanoparticles with appropriate particle distribution.

Experimental methods:

The synthesis of nanoparticles was carried out by a modified hydrothermal method with ultrasound irradiation with iron, zinc, and manganese nitrate precursors and deionized water solvent. The solution was stirred for half an hour under magnetic stirring at room temperature. Then ammonia was added and magnetically stirred for half an hour, and sodium hydroxide solution was added drop by drop and stirred for 10 minutes. Then the solution was exposed to ultrasonic wave radiation for 40 minutes at a temperature of 60 degrees Celsius. Then the mixture was transferred to the autoclave and placed at a temperature of 200 degrees Celsius for 5 hours. After that, the mixture was separated, washed by a centrifuge, and dried at 80 degrees Celsius for 12 hours

Figure 1: Synthesis of nanoparticles by hydrothermal method

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Discussion and conclusion:

The X-ray diffraction pattern is used to study the properties of the crystal structure of the sample, which is shown in Figure 2. As can be seen in Figure 2, the characteristic diffraction peaks at 29.93, 35.40, 36.38, 42.73, 52.46, 56.59, 61.98, and 74.3, which belong to the plates (311), (222), (400), and (422), respectively. (333), (404), and (533) are related, showing the cubic spinel structure and high crystallinity of Zn-Mn ferrite ZnMnFe2O4.

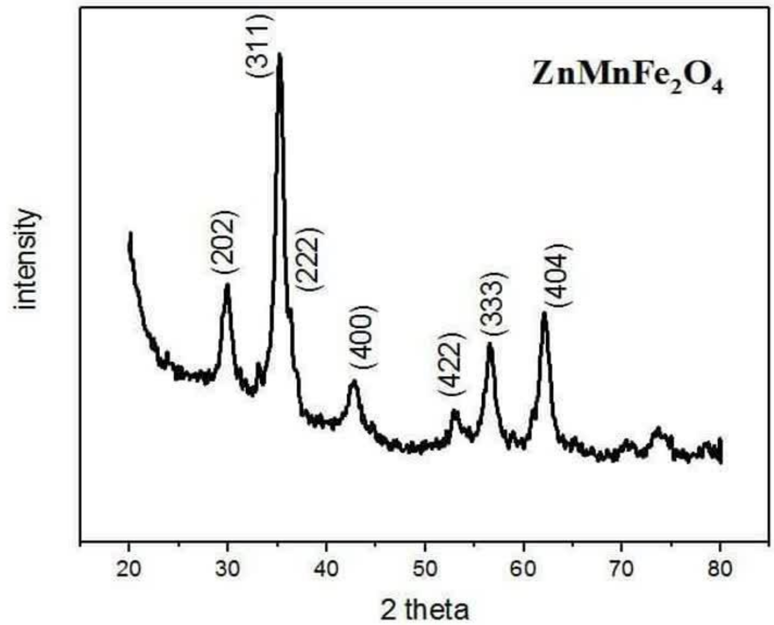

Figure 2: X-ray diffraction pattern for ZnMnFe2O4 nanoparticles

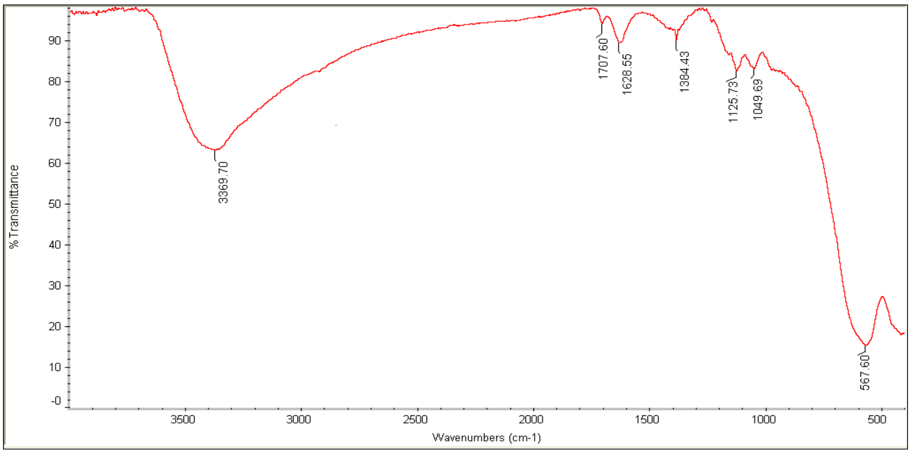

Figure 3: FTIR spectrum of ZnMnFe2O4 nanoparticles

Fourier transform infrared (FTIR) analysis was performed in the range of 400–4000/cm. The IR spectrum is considered an important tool to obtain information about the structure and position of ions in the crystal through the vibrational modes of the crystal. The formation of spinel structures in iron, manganese, and zinc oxide nanoparticles is

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shown in Figure 3. The peaks at 551.56/cm are related to the stretching vibrations of iron-oxygen (Fe-O), and the characteristic peak of the spinel structure of manganese iron and zinc oxide nanoparticles is a strong absorption at 400/cm. The peak at 517 cm is related to the O-Fe-O-Zn bond in the tetrahedral site. Also, the peak at 94/cm corresponds to Mn-O vibrations [12–14]. The peak at 1080/cm is related to O-Fe-O stretching mode, and the peak at 1634/cm is related to Zn-O in the place of octahedral holes in bending vibration. Figure 4 shows the residual loops of the $ZnMnFe2O4$ nanoparticle, which is a measure of the magnetic measurement of the samples. Magnetic curves represent the superparamagnetic behaviour of the sample. The magnetic saturation of nanoparticles is equal to 66.50 emu/g; on the other hand, the value of the coercive field is very small, less than 8 Orsted. This low value confirms the superparamagnetic property of the sample. The high saturation magnetization in this sample guarantees that if a biocompatible coating with an acceptable thickness is placed on this core, the core-shell still has acceptable magnetic properties and can be used as drug delivery. On the other hand, the low coercive field shows that after applying the magnetic field, residual magnetization will not occur in the sample and magnetic particles will not stick together

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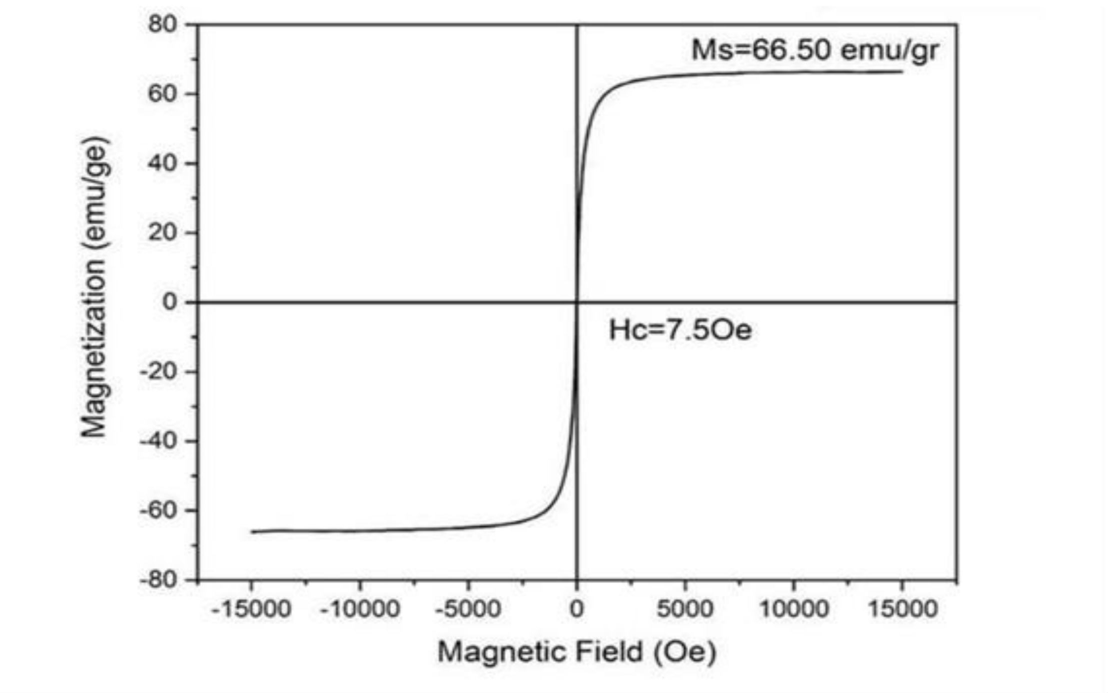

Figure 4: Saturation magnetization curve and coercive field

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Conclusion

Nanoparticles of iron, manganese and zinc oxide were successfully prepared using hydrothermal and sonicchemical methods. X-rays confirmed the formation of Fe-Zn oxide with a cubic spinel structure. Fourier transform infrared analysis and scanning electron microscopy supported the formation of nanoparticles at the nanoscale. The suitable superparamagnetic properties of these nanoparticles make them suitable for their use in drug delivery.

-: References

[1] M.T. Farida et al., Structural, electrical, and dielectric behaviour of NixCo1-xNdyFe2-yO4 nano-ferrites synthesised by the sol-gel method, Dig. J. Nanomater.Biostruct. (2015)

[2] M. Rianne, T. Sembiring, E. Amiruddin, and P. Sebayang, "Materials Science for Energy Technologies: Co-precipitation Synthesis of LaFe 1-x Al x O 3 (x = 0 - 0. 2) on the Structure and Electromagnetic Properties," vol. 6, pp. 43–47, 2023.

[3] L. Fan, X. Guo, X. Hang, and H. Pang, Synthesis of truncated octahedral zinc-doped manganese exacyanoferrates and low-temperature calcination activation for lithium-ion batteries, J. Colloid Interface Sci. (2022).

[4] X. Li, R. Sun, B. Luo, A. Zhang, A. Xia, C. Jin, Synthesis and magnetic properties of manganese-zinc ferrite nanoparticles obtained via a hydrothermal method, J. Mater. Sci. Mater. Electron. (2017)

[5] D. M. et al., "Evaluation of structural and dielectric properties of Mn2+-substituted Zn-spinel ferrite nanoparticles for gas sensor applications," Sensors Actuators, B Chem., vol. 316, no. April 2020.

[6] P. Thakur, D. Chahar, S. Taneja, N. Bhalla, and A. Thakur, A review on MnZn ferrites: synthesis, characterization, and applications, Ceram. Int. (2020).

[7] M. Rianna et al., The effect of Mg-Al additive composition on microstructure, magnetic properties, and microwave absorption on BaFe12 2xMgxAlxO19 (x = 0-0.5) material synthesised from natural iron sand, Mater. Lett. (2019).

[8] L.M. Slavu, R. Rinaldi, and R. Di Corato, Application in Nanomedicine of Manganese-Zinc Ferrite Nanoparticles, Appl. Sci. (Switzerland) (2021).

[9] E.A. Setiadi et al., The synthesis of Fe3O4 magnetic nanoparticles based on natural iron sand by co-precipitation method for the users of the adsorption of Cu and Pb ions, J. Phys.: Conf. Series (2016)

[10] M. Rianna et al., Characterization of natural iron sand from Kata Beach, West Sumatra, with high energy milling (HEM), J. Nat. (2018)

[11] M. Rianna et al., Materials Science for Energy Technologies and Magnetic Properties as a Heavy Metal Adsorbent in Cu, Cr, Mater. Sci. Energy Technol. 6 (2023): 77–80.

[12] J. Wang, K. Zhang, and Y. Zhu, Synthesis of SiO 2-coated ZnMnFe 2O 4 nanospheres with improved magnetic properties, J. Nanosci. Nanotechnology. 5(5) (2005): 772–775.

[13] A Al-Hamaidah, MR Roknabadi, MB Harouni Synthesis of multifunctional superparamagnetic mesoporous ZnMnFe2O4@ Fe–CaSiO3 core-shell for medical applicationsMaterials Chemistry and …, 2023 - Elsevier