



Synthesis of non-stoichiometric zinc ferrite for electromagnetic wave absorber applications



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ABSTRACT

Zn doped Fe_3O_4 nanocrystalline powders are prepared by the Microwave Hydrothermal (M-H) method. The synthesized ferrite powders are characterized using Powder X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), and Vibrating Sample Magnetometry (VSM). Nanocrystalline ferrites of $\sim 10\text{--}20$ nm size are synthesized at a low temperature of 160°C after a treatment time of 60 min. Magnetization studies show the ferrimagnetic nature of the synthesized samples at room temperature. The electromagnetic properties such as complex permittivity and complex permeability spectra are recorded in the frequency range from 1 MHz to 1.8 GHz. The calculated reflection loss indicated that these ferrites show a potential application as multiband electromagnetic wave absorbers.

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1. Introduction

Ferrites are magnetic loss absorbents, which have higher electric and magnetic losses at high frequencies and absorb electromagnetic energy by polarization mechanisms such as hysteresis loss and magnetic domain resonance. Spinel ferrites are of great interest in the electromagnetic applications because they can absorb electromagnetic radiation in microwave bands [1–3]. Magnetic spinel ferrites $[\text{M}(\text{II})\text{Fe}(\text{III})_2\text{O}_4]$; where M represents Co, Mn, Ni, Zn or Fe, etc.] have a face-centred cubic structure with the oxygen ions arranged in a cubic closed-packed lattice. The metal ions can either fill the tetrahedral or octahedral sites. When M occupies the tetrahedral (A) sites the resulting structure is normal and inverse structure when M occupies the octahedral (B) sites. Also, intermediate cases exist where the cations distribute at both sites with a description of $(\text{M}_{1-x}\text{Fe}_x)[\text{M}_x\text{Fe}_{2-x}]\text{O}_4$, where the round and square brackets refer to A sites and B sites respectively and x stands for the inversion degree.

Magnetically, the origin of net magnetic moment in unit formula of the spinel structure is the arithmetic difference between the magnetic moments at A site (upwards) and at B-sites (downwards). Therefore the cation distribution plays an important role

on the magnetic properties of spinel ferrites, [4–6] such as magnetization and magnetic permeability. The control of cation distribution provides a means to tailor their properties. Theoretically, the preferable distribution of various metal cations in spinel ferrites could be predicted by taking the crystal field stabilization energy and ionic radius into the consideration [7]. The results showed that Fe^{2+} , Co^{2+} and Ni^{2+} tend to locate at B sites to form an inverse spinel structure, while Zn^{2+} and Mn^{2+} tend to locate at A sites to form a normal spinel structure [8]. However, in the practical synthesis, mixed distribution of M cations on both A and B sites is always detected when the particle sizes enter into nanoregime or an additional dopant is introduced [9]. Besides, the non-stoichiometric composition of spinel ferrites is found to be an influential factor that induces the inversion degree [10].

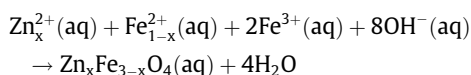
The non-stoichiometric Zn ferrites show superior magnetic properties when compared to the conventional ZnFe_2O_4 . The bulk ZnFe_2O_4 represents a normal spinel, in which Zn^{2+} cations and Fe^{3+} cations are situated at A sites and B sites, exhibiting paramagnetism at room temperature. Whereas inverse spinel ZnFe_2O_4 exhibits ferrimagnetism [11–13]. ZnFe_2O_4 nanoparticles can be synthesized in various methods such as ball milling, coprecipitation, sol-gel and hydrothermal routes [14–16]. Chemical methods offer better control over stoichiometry, particle size and shape of ferrite particles. In this work, non-stoichiometric Zinc ferrite particles prepared by the microwave hydrothermal method and their electromagnetic properties are studied.

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2. Experimental

Reagent grade chemicals of ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Merck, 99.9% pure), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Merck, 99% pure) and zinc chloride (ZnCl_2 , Merck, 99% pure) were dissolved in distilled water and stirred under nitrogen atmosphere to prevent unwanted oxidation of the Fe^{2+} ions in the solution. The molar ratio of powders was adjusted to obtain the composition $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$. After mixing has taken place for 30 min, ammonium hydroxide (NH_4OH , Merck, 99.99% pure) was added drop wise to the reaction mixture to induce formation of the nanoparticles. The pH of the solution was kept at 10 and the reaction allowed to proceed under the same conditions for 1 h. The formation of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ is represented by the following balanced chemical equation:



The precipitate containing some amount of water was then transferred into Teflon-lined vessel (volume 75 ml). The vessel is filled with nitrogen gas and sealed for microwave hydrothermal treatment. We used a microwave digestion system (Model MDS-2000, CEM Corp., Mathews, NC), for hydrothermal treatment, which uses 2.45 GHz microwaves and can operate at 0%–100% full power (630 ± 50 W). After the microwave treatment for 60 min, the products obtained were filtered, and then washed repeatedly with deionized water, followed by freeze-drying overnight.

All the synthesized powders of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ were characterized by X-ray diffraction with a Philips (Panalytical) X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), transmission electron microscopy (Model JEM-2010, JEOL, Tokyo, Japan). The obtained ferrite powders were mixed with 2 wt% polyvinyl alcohol (PVA) as a binder and uniaxially pressed to a pressure of 1500 kg/cm^2 to form pellet and toroidal shape specimens. These green samples are subjected to microwave sintering using a modified microwave oven (2.45 GHz, 1.1 kW). The heating rate was kept at $20 \text{ }^\circ\text{C/min}$ and the cooling rate was maintained at $10 \text{ }^\circ\text{C/min}$ using digital temperature controller (Eurotherm, Model 2416). The green samples were sintered at $900 \text{ }^\circ\text{C}$ for 30 min. Magnetization (M_s) studies were carried out using vibrational sample magnetometer (Lake-shore 665). The bulk densities of the sintered samples were taken by the Archimedes method. The complex permittivity and complex permeability spectra of the samples have been measured in two steps i) in the frequency range from 10 kHz to 1 MHz, an LCR meter, Zentech-3305 (Taipei Taiwan) (ii) the other frequency from 1 MHz to 1.8 GHz Agilent 4291B impedance/material analyzer was used.

3. Results

The XRD pattern of the pure Fe_3O_4 sample synthesized by the Microwave Hydrothermal method is shown in Fig. 1(a). The characteristic peaks at $2\theta = 30.17^\circ$, 35.46° , 43.38° , 53.69° , 57.23° , 62.51° , and 73.87° correspond to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), and (5 3 3) Bragg reflection, respectively agrees with standard magnetite (Fe_3O_4) XRD patterns as in JCPDS file (PDF No. 65-3107). The Fe_3O_4 nanoparticles are of cubic spinel structure and all the other Zn doped Fe_3O_4 samples also exhibit the same cubic spinel structure. The XRD patterns of sintered samples (Fig. 1(b)) show improved crystallinity and smaller line widths in the XRD pattern than that of the corresponding nanopowders. The patterns display sharp and well-resolved diffraction peaks, revealing the high crystallinity of the samples. No additional peaks due to any impurity phases were detected.

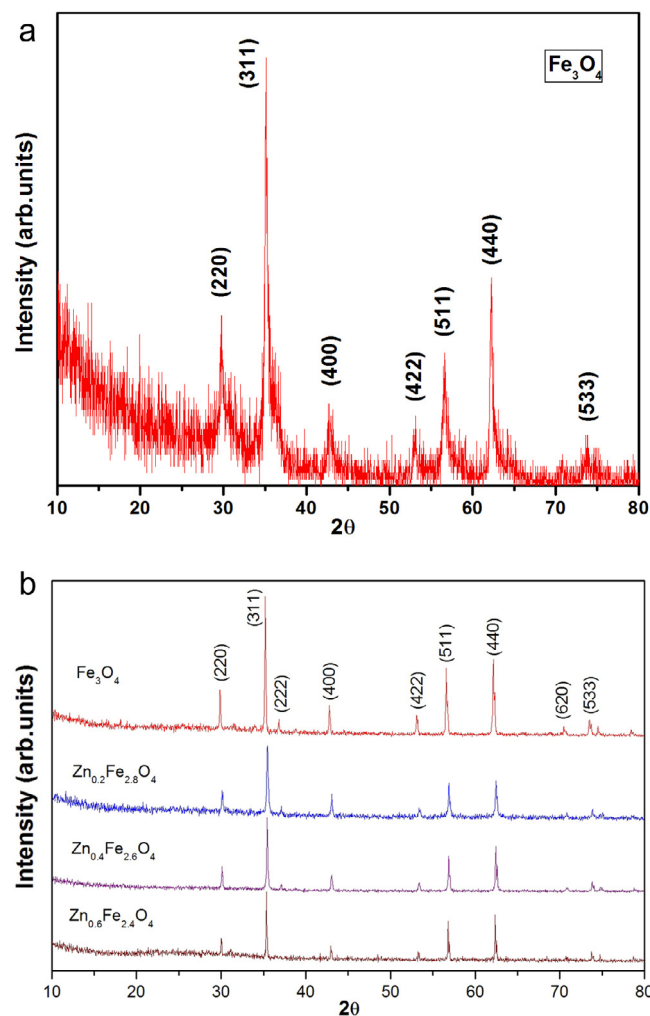


Fig. 1. (a) XRD pattern of as synthesized Fe_3O_4 . (b) XRD pattern of microwave sintered $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$.

Table 1
Crystallite size, lattice parameter and bulk density of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$.

Sample	Crystallite size (D) nm	Lattice parameter (a) \AA	Bulk density (d_b) g/cm^3
$x = 0.0$	15	8.369	4.5
$x = 0.2$	19	8.371	4.7
$x = 0.4$	21	8.382	4.9
$x = 0.6$	25	8.391	5.1

Table 1 gives the calculated values of crystallite size (D), lattice parameter (a), and bulk density (d_b). The average crystallite size of nanoparticles is calculated from the full-width-at-half maximum (FWHM) of high intense (3 1 1) diffraction peak using Scherrer's equation. The particle size of as synthesized powders is in the range 15–25 nm. The lattice parameter for the $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ increases from 8.369 to 8.391 \AA as Zn^{2+} doping increases from $x = 0$ to $x = 0.6$. This is due to the doped Zn^{2+} (ionic radius 74 pm) ions may replace the Fe^{3+} (64 pm) ions at the A site and Fe^{2+} (70 pm) ions at the B-site as a result the crystal lattice expands. The bulk density of the undoped sample is smaller than the Zn doped samples indicating that it is slightly porous material. The increase in bulk density with Zn content shows the decrease of porosity of the samples. Fig. 2 shows TEM images of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ for $x = 0.4$. It is clear from the image that the synthesized powders

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