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# Unique electromagnetic properties of the zinc ferrite nanofiber

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#### ARTICLE INFO

### ABSTRACT

shape anisotropy.

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behavior [7] electrical characteristics [9] and comiconductor

The ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle and nanofiber were synthesized by electrospinning method. The phase

composition, morphology, magnetic and electromagnetic properties were analyzed. The results showed

that both the samples exhibited a pure phase of spinel type ferrite. The  $ZnFe_2O_4$  ferrite nanoparticle was

aggregated, while the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber performed the homogeneous nano-fibrous shape as well

as single-particle-chain structure. The magnetic analysis indicated that the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber

showed ferromagnetic behaviour. Moreover, the dielectric loss and magnetic loss properties of ZnFe<sub>2</sub>O<sub>4</sub>

ferrite nanofiber were both enhanced due to its better dipole polarization, interfacial polarization and

## 1. Introduction

Ferromagnetic resonance and dielectric relaxation are wellknown mechanisms normally responsible for microwave absorption [1,2]. However, Zinc ferrite,  $ZnFe_2O_4$ , is not among the high efficient microwave absorbing material candidates because of its paramagnetic property and poor dielectric loss ability. To improve the electromagnetic properties of  $ZnFe_2O_4$  ferrite in the GHz frequency, a common approach was to change the ions distribution between the A-site and B-site in the spinel structure via doping magnetic ions. For example, the ferromagnetic properties were discovered in the Ni<sup>2+</sup>-doped, Co<sup>2+</sup>-doped and Mn<sup>2+</sup>doped  $ZnFe_2O_4$  ferrite [3–5]. However, the dielectric loss cannot be evidently enhanced, meanwhile the doping process was easy to introduce impurity and damage the spinel structure.

Here, one-dimension nanostructure was adopted to directly improve the electromagnetic properties of  $ZnFe_2O_4$  ferrite. By comparing with the morphology, magnetic and electromagnetic properties between the zinc ferrite nanoparticle (NP) and nanofiber (NF), we demonstrate that the single-particle-chain structure has more interface than single particle. The dielectric loss and magnetic loss properties of the spinel ferrite nanofiber were both enhanced due to its better dipole polarization, interfacial polarization and shape anisotropic. This study may also expand the applications of  $ZnFe_2O_4$  into new areas in gas sensing [6], magnetic

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#### 2. Experimental

The ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle and nanofiber were synthesized by the electrospinning method. First, the metal salt solution was prepared by dissolving the 0.01 mol C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>Zn · 2H<sub>2</sub>O and 0.02 mol FeCl<sub>3</sub> · 6H<sub>2</sub>O into the 20 ml N,N-dimethylformamide (DMF). Second, different amount polyvinylpyrrolidone (PVP, K-30) was added in 36 ml anhydrous alcohol to prepare the PVP solution. To obtain the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle, the amount of PVP was 5.0 g. While, the 9.0 g PVP was using to prepare the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber. Then, the spinning solution was obtained after the as-prepared metal salt solution and PVP solution were mixed and stirred for 5 h. Third, the spinning solution was electrospun to prepare the precursor. The applied positive voltage was 12 kV, the feed rate was 3 ml/h, and the distance from needle tip to collector was 13 cm. Finally, the precursor were dried at 80 °C for 7 h and then calcined at 700 °C for 2 h with a heating rate of 2 °C/min.

The X-ray diffraction analysis was carried out using an X-ray powder diffractometer (XRD, Rigaka, D/MAX2500). The morphology was observed using a transmission electron microscope (TEM, FEI Tecnai G2 F30) and a field emission scanning electron microscopy (FE-SEM, HITACHI S-4800). Magnetic properties were tested by vibrating sample magnetometer (VSM, Lakeshore 7307–9309). The electromagnetic parameters ( $\varepsilon'$ ,  $\varepsilon''$ ,  $\mu'$ ,  $\mu''$ ) were measured by a Network analyzer (Agilent PNA 8363B) in the frequency range of





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2–18 GHz. The samples were prepared by uniformly mixing 85 wt% of paraffin and 15 wt% of ferrite nanofiber, and then pressed in a cylindrical mold with a size of 3 mm (inside) × 7 mm (outside) × 2 mm (height). The measured values of reflected and transmitted scattering parameters ( $S_{11}$ ,  $S_{21}$ ) were used to determine the electromagnetic parameters [10].

#### 3. Results and discussion

The phase composition is identified by the XRD. From Fig. 1, there is no impurity phase presented in the spectra, and all the diffraction peaks can be indexed to the zinc ferrite (JCPDS No. 65-3111). It is indicated that both the as-synthesized  $ZnFe_2O_4$  ferrite nanoparticle and nanofiber have a pure phase of spinel ferrite.



Fig. 1. XRD spectra of the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle and nanofiber.

Morphologies of samples were measured by FE-SEM and TEM. As shown in Fig. 2(a), the as-prepared  $ZnFe_2O_4$  ferrite nanoparticle was aggregated, and the nanoparticle size was nearly 80 nm. For the  $ZnFe_2O_4$  ferrite nanofiber, it can be seen from Fig. 2(b) that the sample exhibited the typical and homogeneous nano-fibrous shape as well as high length-diameter ratio. The diameter of the nanofiber was about 80 nm. The TEM analysis indicated that the as-prepared  $ZnFe_2O_4$  ferrite nanofiber possessed single-particlechain structure, and there were many interfaces among the single particles (Fig. 2(c)). From Fig. 2(d), the HRTEM image revealed that the spinel ferrite phase was highly crystallized. The spacing values of 0.25 nm depicted the lattice-resolved (311) crystalline plane.

The magnetic property of the  $ZnFe_2O_4$  ferrite nanofibers was determined by VSM at room temperature, and its hysteresis loop was presented in Fig. 3. It is striking to note that the  $ZnFe_2O_4$ 



Fig. 3. Magnetic hysteresis loop of the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber at room temperature.



Fig. 2. (a) FE-SEM image of ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle, (b) FE-SEM image, (c) TEM image, (d) HRTEM image of ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanopfiber.



Fig. 4. (a) Dielectric loss factor and (b) magnetic loss factor of ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle and nanofiber.

ferrite nanofibers behave as a significant hysteresis loop, indicating the ferromagnetic property. As well known, the traditional ZnFe<sub>2</sub>O<sub>4</sub> ferrite particle usually shows paramagnetic property. However, previous studies have confirmed that the nanocrystalline ZnFe<sub>2</sub>O<sub>4</sub> could exhibit ferromagnetic property due to the effects of small grain size on the cation distribution and magnetic properties [11,12]. Here, our research also in conformity with these studies. The saturation magnetization ( $M_s$ ) was nearly 12.4 emu/g and the coercivity ( $H_c$ ) was about 48.79 Oe.

To investigate the electromagnetic loss properties, the dielectric loss property and magnetic loss property were usually characterized by dielectric loss factor  $(\tan \delta_{\varepsilon} = \varepsilon'' / \varepsilon')$  and magnetic loss factor (tan  $\delta_u = \mu'' | \mu'$ ), respectively [13,14]. The  $\varepsilon'$  and  $\varepsilon''$  are the real part and the imaginary part of the complex permittivity, and the  $\mu'$  and  $\mu''$ are the real part and the imaginary part of the complex permeability, respectively. The complex permittivity and the complex permeability of the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle and nanofiber were investigated in the frequency range of 2-18 GHz, and the results were shown in Fig. S1. Then, the dielectric loss factor and magnetic loss factor were calculated. From Fig. 4(a), the dielectric loss factor of ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle was nearly 0.01-0.06. However, the dielectric loss factor of ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber was increased to 0.09–0.12. This value was also larger than that of the Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> octahedral nanoparticle (0.00-0.06) and NiZn-ferrite nanocrystallines (0.01-0.09) [15,16]. It can be ascribed to the following three reasons. First, the migration between the  $Fe^{3+}$  and  $Zn^{2+}$  ions can introduce the intrinsic electric dipole, causing the dipole polarization in the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber. Second, the orientational polarization can be improved due to the large shape anisotropic [17]. Third, the single-particle-chain structure has more interface than single particle, and the interfacial polarization was beneficial for the attenuation of microwave power.

Moreover, it can be found from Fig. 2(b) that the magnetic loss property of ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber was also stronger than which of ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle. In generally, natural resonance of ferrite was the main mechanism for the magnetic loss. According to the Larmor equation, natural-resonance frequency ( $f_r$ ) can be expressed as:  $f_r = (\gamma H_a)/2\pi$ , where  $\gamma$  is the gyromagnetic ratio and  $H_a$  is the effective anisotropic field [18]. The effective anisotropic field of the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber was enhanced due to its high length–diameter ratio and large shape anisotropic. As a result, the ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber performed stronger magnetic loss property.

#### 4. Conclusion

The ZnFe<sub>2</sub>O<sub>4</sub> nanoparticle and nanofiber with a pure phase of spinel type ferrite were successfully synthesized by the

electrospinning method. The ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber exhibited the unique single-particle-chain structure and behaved as the ferromagnetic property. The dielectric loss and magnetic loss properties of ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber were both stronger than that of ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanoparticle due to its better dipole polarization, interfacial polarization and shape anisotropic. This work gives a novel insight to improve the electromagnetic properties of ferrite, and the as-prepared ZnFe<sub>2</sub>O<sub>4</sub> ferrite nanofiber can be potentially used as a lightweight microwave absorbing material.

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#### Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.03.049.

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