Preparation of Ferrite Fe$_3$O$_4$ and Its Electromagnetic Wave Absorption Properties

Fuli Yang$^1$, Xingzhe Hou$^1$, Lirui Wang$^2$, Youjiang Li$^2$ and Miao Yu$^2$, *

$^1$Electric power research institute, Chongqing Electric Power Corporation, State Grid, Chongqing China
$^2$College of Optoelectronic Engineering, Chongqing University, Chongqing China

*Corresponding author’s e-mail: yumiao@cqu.edu.cn

Abstract. Ferrite materials have good frequency characteristics. Their relative permeability is large and relative permittivity is small. These make it suitable for matching layer and have a good application prospect in broadening the absorption bandwidth. In this paper, ferrite was prepared by a simple chemical precipitation-dehydration method, and the ferrite Fe$_3$O$_4$ particles with 40% mass fraction were mixed with paraffin to form a ring test sample. The experimental results show that the as-prepared sample at higher temperatures has more stable nucleation and fewer defects, so it has more significant electromagnetic wave absorption performance. The minimum reflection loss is about -44 dB, and the electromagnetic absorption band with the reflection loss RL less than -10 dB is located at 12.5-14.1 GHz (3 mm) and 6.5-8.1 GHz (5 mm), respectively.

1. Introduction
Excessive electromagnetic waves cause serious damage to human organs such as human eyes and central nervous system [1, 2]. United Nations Conference on the human environment has listed electromagnetic radiation as one of the major pollutants. In particular, the proliferation of electronic and communication equipment has increased the density of electromagnetic energy in confined spaces, and electromagnetic interference and pollution have become more and more serious [3]. At the same time, radar detection technology seriously threatens the survivability and combat effectiveness of battlefield weapons [4, 5]. Therefore, both electromagnetic protection and electromagnetic stealth technology are urgent issues that we are currently facing, and the core issue is the development of electromagnetic wave absorbing materials.

Ferrite is a kind of double complex dielectric material with both magnetic and dielectric properties, which has both electrical loss and magnetic loss for electromagnetic wave loss. Due to high resistivity ($10^8$-$10^{12}$), ferrite can avoid skin effect of metal conductor at high frequency, so it can still maintain high permeability at high frequency. At the same time, ferrite also has a wide range of raw materials and low price characteristics. The research on ferrite absorbing materials has achieved outstanding results and has also been applied to some practical engineering fields. However, the absorbing properties (such as absorption strength, bandwidth, etc.) of the ferrite material and the preparation process still need to be further improved.
In this paper, ferrite Fe₃O₄ particles were prepared by simple chemical precipitation-dehydration method. Ferrous chloride (FeCl₂) and ferric chloride (FeCl₃) were iron sources. Compared with other common methods, such as sol-gel method, this method has the advantages of simple operation, short preparation period and low cost. Meanwhile, ferrite Fe₃O₄, with thin absorbing coating thickness, can achieve significant electromagnetic wave absorption in a wide frequency band. The loss mechanism of ferrite Fe₃O₄ was also studied in-depth.

2. Experiment

2.1. Raw material
Ferrous chloride (FeCl₂) and ferric chloride (FeCl₃), analytical grade, Tianjin kemio Chemical Reagent Co., Ltd.; Sodium hydroxide (NaOH), analytical grade, Chengdu Kelong Chemical Reagent plant; deionized water, were self-made in the laboratory.

2.2. Preparation of ferrite Fe₃O₄
First, Excess NaOH powder was dissolved in 100 ml of deionized water. Then, ferrous chloride (FeCl₂) and ferric chloride (FeCl₃) were weighed according to a molar ratio of n(FeCl₃):n(FeCl₂)=1:2, and they were poured into 200 ml of deionized water to prepare a homogeneous solution. Thereafter, the NaOH solution and the mixed solution containing iron ions were simultaneously slowly dropped into the reaction tank, and the water bath control temperature was maintained at 25 °C (sample S1) or 80 °C (sample S2), respectively. The reaction system was then gently stirred. After the reaction was completed, it was allowed to stand for 10 h. The obtained product was washed several times with deionized water and absolute ethanol, suction filtered, and dried in a vacuum oven at 80 °C for 6 h. Finally, the final product Fe₃O₄ particles are obtained.

2.3. Testing and characterization
The elemental composition, crystal structure and morphology of the particles are detected by vega2 X-ray spectrometer (EDS), X-ray diffraction XRD and scanning electron microscope (SEM), respectively.

Ring-shaped samples having an outer diameter of 7 mm, an inner diameter of 3.04 mm, and a thickness of 2 to 5 mm were pressed by paraffin-bonding 40 wt% of ferrite Fe₃O₄. The relative permeability and permittivity of the samples were tested by coaxial reflection/transmission technique using an Agilent 85071E vector network analyzer. The test range is from 2 to 18 GHz.

2.4. Calculation of absorption performance
According to the transmission line theory, for single-layer absorbing materials with metal as the back plate, the reflection loss (RL) can usually be calculated by the following formula [6-8]:

\[
Z_{in} = \sqrt{\frac{\mu_0 \mu_r}{\varepsilon_0 \varepsilon_r}} \tanh\left( j \frac{2\pi c}{f} \sqrt{\mu_r \varepsilon_r} \right)
\]

(1)

\[
L = 20 \log_{10} \left| \frac{Z_m - Z_0}{Z_m + Z_0} \right|
\]

(2)

Where \(Z_0\) is the impedance of free space, \(Z_{in}\) is the input impedance between free space and the material interface, \(c\) is the speed of light, \(f\) is the frequency of the microwave, and \(d\) is the thickness of the absorbing material.
3. Results and discussion

3.1. Characterization of the samples

It can be seen from the figure 1 that the diffraction peaks are located at $2\theta=30.1^\circ$, $35.6^\circ$, $43.1^\circ$, $53.5^\circ$, $57.1^\circ$, $62.7^\circ$, respectively, corresponding to (220), (311), (400), (422), (511), (440) crystal planes. This matches the cubic spinel structure magnetite (JCPDS card 19-0629) [2].

![Figure 1. XRD image of ferrite Fe$_3$O$_4$](image)

From SEM, the surface of ferrite Fe$_3$O$_4$ particles is rough and uneven, and has an irregular circle shape with a diameter of about 1-3 μm. The main elements are Fe and O. Cl and Na are reagents remaining and C might be mixed during scanning electron microscope operation.

![Figure 2. SEM and EDS images of ferrite Fe$_3$O$_4$ (a-c is a different multiple of SEM and EDS images for sample S1; d-f is a different SEM and EDS images for sample S2).](image)

3.2. Electromagnetic parameters and microwave absorption properties

The electromagnetic losses are closely related to complex permittivity and permeability. Figure 3a showed the relationship of complex permittivity of ferrite Fe$_3$O$_4$ with frequency. In 2-12 GHz, the complex permittivity of sample S1 and sample S2 is almost unchanged. Above 16 GHz, the complex permittivity of the samples fluctuated slightly with the frequency. However, in 12-16 GHz, the complex permittivity fluctuated greatly, and the valley and peak values appeared in 13-14 GHz. According to dielectric loss tangent ($\tan\sigma_E=\varepsilon''/\varepsilon'$, as shown in figure 4a), ferrite had a strong dielectric loss capability at 13-15 GHz. Due to the presence of Fe2+ and Fe3+ valence ions in the ferrite, electric dipole polarization loss was formed in the alternating electromagnetic field.

From figure 3b, the real part of complex permeability $\mu'=0.72 \sim 1.2$, the imaginary part of complex permeability $\mu''=0.04 \sim 0.46$. The peak and valley value of the complex permeability appeared near 4 GHz, 7 GHz and 14 GHz. Based on magnetic loss tangent ($\tan\sigma_M=\mu''/\mu'$, as shown in figure 4a), there was strong magnetic loss capacity near the corresponding frequency, which was mainly caused by the natural resonance loss of ferrite.
Figure 3. Complex dielectric constant and complex permeability $\mu$ of Fe$_3$O$_4$ (samples S1 and S2)

Polarization hysteresis between interfaces will produce dielectric loss with the change of frequency [9]. However, there were Fe$^{2+}$, Fe$^{3+}$ valence changing ions in ferrite, so it was believed that the ferrite Fe$_3$O$_4$ had better dielectric loss. Debye dipole relaxation is an important mechanism for dielectric loss [10]. According to the transmission line theory, permittivity can be expressed by the following formula [11,12]:

$$\left(\frac{\varepsilon' - \varepsilon_\infty + \varepsilon_\infty}{2}\right)^2 + \left(\varepsilon''\right)^2 = \left(\frac{\varepsilon_\infty - \varepsilon_\infty}{2}\right)^2$$

(3)

According to formula (3), the curve of the real and imaginary parts of permittivity is a semicircle called Cole-Cole semicircle. Each Cole-Cole semicircle corresponds to a Debye relaxation process [13,14]. Both samples had a Cole-Cole semicircle. However, the Cole-Cole semicircle of sample S1 was relatively smooth, while the Cole-Cole semicircle of sample S2 was twisted obviously. This indicates that other loss mechanisms (such as electron polarization, conductivity loss and oxygen defect) also contribute greatly to sample S2.

Figure 4. Electromagnetic loss tangent of ferrite Fe$_3$O$_4$ a; Cole-Cole semicircle b, c; with the value of $\mu''(\mu')^{-f^{-1}}$ varies with frequency in 2~18GHz.

The magnetic loss of ferrite Fe$_3$O$_4$ mainly comes from hysteresis, eddy current loss and natural resonance in 2-18GHz [15]. The hysteresis is caused by irreversible magnetization and is negligible under weak external magnetic field [16]. As can be seen from formula $\mu'' \approx 2\mu_0(\mu')^2\sigma d^2/3$, eddy current loss is related to the diameter $d$ and conductivity $\sigma$ of metal particles, here $\mu_0$ is the vacuum permeability [17,18]. If the magnetic loss of the absorbing material was only due to the eddy current loss, the value of $C_0 = \mu''(\mu')^{-f^{-1}}$ should remain constant when the frequency changed [19]. However, the value of $C_0$ of ferrite fluctuated in 2-18 GHz. In other words, the effect of eddy current on their permeability can be ignored, and the magnetic loss of prepared ferrite mainly come from natural resonance.
The reflection loss (RL) curve of the samples with different thickness was shown in figure 5. As is known to all, the reflection loss value $RL < -10$ dB (corresponding to 90% microwave absorption) is the target value of EM absorber in practical application. The reflection loss value and absorption bandwidth of sample S2 were better than that of sample S1. This might be because the nucleation of sample S2 was relatively more stable and the crystal nucleus defects were less. For sample S2, double absorption peaks occurred at 6-8 GHz and 13-15 GHz. When the thickness of the sample S2 was 2 mm, the minimum reflection loss reached -44 dB with bandwidth of 1.6 GHz at 6.5-8.1 GHz. While the thickness of the sample S2 continued to increase to 5 mm, the minimum reflection loss reached -43 dB with bandwidth of 1.6 GHz at 12.5-14.1 GHz.

**Figure 5.** Reflection loss of ferrite $\text{Fe}_3\text{O}_4$ with thickness of 2-5mm (a. Sample S1; b. Sample S2)

4. Conclusion
Ferrite $\text{Fe}_3\text{O}_4$ absorber particles were successfully prepared by chemical precipitation-dehydration method in this paper. The prepared ferrite has both magnetic loss and dielectric loss. From the electromagnetic loss angle, Debye relaxation and natural resonance, the principle of absorption loss was systematically studied, which would provide a basis for future research on ferrite absorbing materials. The ferrite sample S2 prepared at 80 $^\circ$C had good electromagnetic wave absorption with the minimum reflection loss of -44 dB. Moreover, its absorption bandwidth reached 1.6 GHz. The high absorption ability and wide absorption band indicated that the effectiveness of the ferrite $\text{Fe}_3\text{O}_4$ absorbing particles in the field of electromagnetic stealth and electromagnetic protection. In addition, the flexible and convenient preparation method provided a new strategy for the preparation of other ferrite particles.

Acknowledgments
The financial support from Electric power research institute of Chongqing Electric Power Corporation of State Grid (52202317001D) is highly acknowledged.

References
[1] Lv H, et al. Porous Three-Dimensional Flower-like Co/CoO and Its Excellent Electromagnetic Absorption Properties. [J]. ACS Applied Materials & Interfaces, 2015, 7(18):9776-9783
[2] Wang Z, et al. Enhanced microwave absorption of Fe3O4 nanocrystals after heterogeneously growing with ZnO nanoshell. [J]. RSC Advances, 2013, 3(10):3309-3315
[3] Zhao B, et al. Preparation and electromagnetic wave absorption properties of novel dendrite-like NiCu alloy composite [J]. RSC Adv, 2015, 5(53): 42587-42590
[4] Zhao B, et al. Facile synthesis and novel microwave electromagnetic properties of flower-like Ni structures by a solvothermal method.[J]. Journal of Materials Science: Materials in Electronics, 2014, 25(8):3614-3621
[5] Liu T, et al. Microporous Co@CoO nanoparticles with superior microwave absorption properties[J]. Nanoscale, 2014, 6(4): 2447-2454
[6] Shi X, et al. Dual nonlinear dielectric resonance and nesting microwave absorption peaks of hollow cobalt nanochains composites with negative permeability[J]. Applied Physics Letters, 2009, 95(16):163108-1 -163108 -3
[7] Beshkar F, J.H.M.M, et al. Dendritic a-Fe2O3 nanostructures: facile hydrothermal synthesis,
characterization and microwave absorption. Journal of Materials Science Materials in Electronics, 2016. 12(27): 1-7

[8] Biswas S, G P Kar and S Bose, et al. Attenuating microwave radiation by absorption through controlled nanoparticle localization in PC/PVDF blends. Phys Chem Chem Phys, 2015. 17(41): 27698-712

[9] Zhuo R.F, et al. Multistep Synthesis, Growth Mechanism, Optical, and Microwave Absorption Properties of ZnO Dendritic Nanostructures. The Journal of Physical Chemistry CJ. Phys. Chem. C, 2008, 112(31): 11767-11775

[10] Zhao B, et al. Synthesis of flower-like CuS hollow microspheres based on nanoflakes self-assembly and their microwave absorption properties. JOURNAL OF MATERIALS CHEMISTRY A, 2015, 3(19): 10345-10352

[11] Zhu W, et al. Electromagnetic and microwave-absorbing properties of magnetic nickel ferrite nanocrystals. NANOSCALE, 2011, 3(7): 2862-2864

[12] Zhao B, et al. Synthesis of flower-like CuS hollow microspheres based on nanoflakes self-assembly and their microwave absorption properties. J. Mater. Chem. A, 2015, 3(19): 10345-10352

[13] Fang P H, et al. Cole—Cole Diagram and the Distribution of Relaxation Times. The Journal of Chemical Physics, 1965, 42(10): 3411-3413

[14] Du Y, et al. Shell Thickness-Dependent Microwave Absorption of Core–Shell Fe3O4@C Composites. ACS Applied Materials & Interfaces, 2014, 6(15): 12997-13006

[15] Yu M, et al. Flower-like carbonyl iron powder modified by nanoflakes: Preparation and microwave absorption properties. Applied Physics Letters, 2015, 106(16): 161904

[16] Wu M, et al. Microwave magnetic properties of Co50/(SiO2)50 nanoparticles. Applied Physics Letters, 2002, 80(23): 4404-4406.

[17] Murali K P, et al. Structure-magnetic property correlations in nickel-polymer nanocomposites. Journal of Materials Science: Materials in Electronics, 2016, 27(1): 154-162

[18] Wu M, et al. Microwave magnetic properties of Co[sub 50]/(SiO[sub 2])[sub 50] nanoparticles. Applied Physics Letters, 2002, 80(23): 4404.

[19] Wang Z, et al. Magnetic and microwave absorption properties of self-assemblies composed of core-shell cobalt-cobalt oxide nanocrystals. Phys Chem Chem Phys, 2015. 17(5): 3796-801.