Microwave Electromagnetic and Absorption Properties of AFe2O4(A=Ni,Mn,Zn) Ferrites

Jie Huang, Yuan Liu, Ying Li and XiangXuan Liu

ABSTRACT
The spinel ferrite (AFe2O4, A=Ni, Zn, Mn) were prepared under the same condition via sol–gel method. The structure and electromagnetic properties of the powders were characterized by X-ray diffractometer, scanning electron microscope, and vector network analyzer, respectively. These materials were found to be very good catalysts for the oxidation of styrene to benzaldehyde in the presence of hydrogen peroxide. Because of the difference in radius and electrical of these ions (Ni2+, Zn2+ and Mn2+), the ion distribution of ferrites were diverse, so that the electromagnetic parameters and absorbing properties varied. After analyze the contour map of the attenuation constant \( \alpha \) and reflectivity \( R \), it shows that the absorbing weak point of NiFe2O4 lies in the high frequency range 8-14GHz ,the absorbing properties of MnFe2O4 is relatively balanced, and the absorbing capacity of ZnFe2O4 in the high-frequency part is poor. NiFe2O4, MnFe2O4 and ZnFe2O4 in absorbing band complement each other very well. By preparing an appropriate proportion of Ni-Mn-Zn composite spinel ferrite, an excellent absorbing agents will be expected.

1 INTRODUCTION
The development of microwave-absorbing materials continues to attract much attention with the increasing of electromagnetic pollution and the stealth technology for military platforms [1]. Among the spinel type ferrites, nickel ferrite is a widely used material for microwave applications due to its high Curie temperature and good temperature stability of saturation magnetization [2].

However, It is well known that the magnetic and electrical properties of AFe2O4 nanoparticles can be varied by changing the identity of the divalent A2+ (A=Ni, Mn, Zn) cation or by partial substitution, while maintaining the basic crystal structure[3-5]. Much studies have been carried out for synthesis of AFe2O4 (A=Ni, Mn, Zn), focus on the effects of the synthesis conditions (solvents/ligands, temperature and reaction time) and its magnetic property, rarely been involved in the change of its electromagnetic properties study among the different divalent A2+ (A=Ni, Mn, Zn) cation. Therefore, the aim of this paper is the development of microwave-absorbing materials based on
AFe_{2}O_{4}(A=\text{Ni, Mn, Zn}) ferrites using the sol-gel method and investigation of their absorption characteristics like dielectric constant, dielectric loss, permeability and so on.

2 EXPERIMENTAL
2.1 Synthesis of AFe_{2}O_{4}(A=\text{Ni, Mn, Zn})

AFe_{2}O_{4} (A=\text{Ni, Mn, Zn}) spinel ferrites were prepared by a sol-gel-auto combustion method. According to AFe_{2}O_{4} (A=\text{Ni, Mn, Zn}), stoichiometric amounts of A(NO_{3})_{2} and Fe(NO_{3})_{3} were dissolved in distilled water and an appropriate amount (1:1 mol ratio of citric acid to NO_{3}^{-}) of citric acid was added to complex the metal ions completely according to the composition of AFe_{2}O_{4}. Maintaining the pH at 7.0 by slow addition of ammonia solution (25 wt%). The solution was evaporated at 80°C until a viscous gel formed, then air-dried at 120°C, ignited in air, and burned into dendritic powders. Finally, the precursor powder was sintered at 1200°C for 3h.

2.2 Measurement of the properties

The phase structure was identified by XRD(D/max-IIB, Japan). VEGA II XMU INCA SEM was employed for morphological analysis. SEM parameters (complex permeability and permittivity) were measured using a vector network analyzer (HP-8720ES) in the frequency range of 2-18 GHz.

3 RESULT AND DISCUSSION
3.1 XRD analysis

Figure 1 gives the results of the density and the particle size determined by XRD. The samples were all annealed at 1200°C for 3h. XRD analysis shows that in the present experimental conditions we have obtained crystalline AFe_{2}O_{4} samples with the expected cubic spinel structure, agree with the corresponding reported JCPDS data (Card Nos. NiFe_{2}O_{4}:71-1269; ZnFe_{2}O_{4}:02-1043, MnFe_{2}O_{4}:02-1392). No other impurity peaks appear, and the shape of diffraction peak of all facets is sharp, relative strength, it is a description that crystals tend to complete at this time, and the pure AFe_{2}O_{4} powder is generated.

Figure 2 shows SEM images for the AFe_{2}O_{4}(A=\text{Ni, Mn, Zn}) spinel ferrites prepared at 1200°C for 3h in air. It is clearly shown that the MgFe_{2}O_{4} are usually in a spherical shapes with smooth surfaces, and have a narrow size distribution. These samples are uniform with diameters of about 300 and 800 nm, respectively.

![XRD patterns of AFe_{2}O_{4}(A=\text{Ni, Mn, Zn}) spinel ferrites.](image-url)
As shown in Figure 2 for different ion replacement composite nickel ferrite powder SEM image. It can be seen from Figure 1, the outline of NFe2O4 powders and ZnFe2O4 the powder is very smooth, like a grain of rice, the size of most of particles is in the 1μm or so. The edges of particles of the MnFe2O4 powder and is apparent and sharp into polyhedral shapes, the particle size of the former is larger, at around 3μm, the particle size of the latter is smaller, mostly in 1.5μm, a small amount of them is more than 1.5μm.

![Figure 2. SEM micrographs of AFe$_2$O$_4$ (A=Ni, Mn, Zn) spinel ferrites.](image)

### 3.2 Complex permittivity and permeability of AFe$_2$O$_4$

![Figure 3. The complex permittivity (a,b) and complex permeability(c,d) of AFe$_2$O$_4$ (A=Ni, Mn, Zn) spinel ferrites.](image)

Figure 3 shows the complex permittivity of AFe$_2$O$_4$ (A=Ni, Mn, Zn) spinel ferrites. Figure 3(a) and (b) respectively show the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the permittivity of the specimens plotted as a function of 2–18GHz. $\varepsilon'$ and $\varepsilon''$ represent the energy storage ability and loss ability respectively. Which can be seen from Figure 3: NiFe$_2$O$_4$ and Co Fe$_2$O$_4$ sample the real part of the complex permittivity $\varepsilon'$ and the magnitude of the imaginary part $\varepsilon''$ close to the same change trend. The $\varepsilon'$ located in
between 3.0 to 4.6, an apparent resonance peak appears in the range of 15-18GHz; $\varepsilon''$ is essentially unchanged in the 2-14GHz, the distribution of values around 0.2, in 14-18GHz of between an obvious formant. The NiFe$_2$O$_4$ real and imaginary parts of the complex permittivity are greater than CoFe$_2$O$_4$. The MnFe$_2$O$_4$ and ZnFe$_2$O$_4$ samples the real part of the complex permittivity $\varepsilon'$ trend is significantly larger than the NiFe$_2$O$_4$ and CoFe$_2$O$_4$ sample complex permittivity of the real part of $\varepsilon'$ distribution between 6.5 to 10.0. When it comes to beyond the 6GHz, The ZnFe$_2$O$_4$ sample complex permittivity of the real part of $\varepsilon'$ is bigger than the MnFe$_2$O$_4$. 2-15GHz, MnFe$_2$O$_4$ complex permittivity of the imaginary part of $\varepsilon''$ value fluctuations, the formant apparent in 15-18GHz; ZnFe$_2$O$_4$ by the complex permittivity of the imaginary part of $\varepsilon''$ value fluctuations, the formant apparent in 3-4GHz and 13-14GHz.

The real ($\mu'$) and imaginary ($\mu''$) parts of the permeability are shown in Figure 3(c) and (d), respectively. As can be seen by Figure 3, the NiFe$_2$O$_4$ sample complex permeability real part $\mu'$ in the 2-6GHz Movement the downward trend, 6-18GHz gradually increases; imaginary part $\mu''$, 10-18GHz substantially decreases gradually between 10GHz remain unchanged. CoFe$_2$O$_4$ sample the real part of the complex permeability $\mu'$ tended to increase in the 2-4GHz, constant thereafter; imaginary part $\mu''$ was a significant downward trend between the 2-18GHz. The MnFe$_2$O$_4$ and ZnFe$_2$O$_4$ samples the real part of the complex permittivity $\varepsilon'$ trend, significantly larger than the NiFe$_2$O$_4$ and CoFe$_2$O$_4$ sample complex permittivity of the real part of $\varepsilon'$ distribution between 6.5-10.0. 6GHz, ZnFe$_2$O$_4$ by sample complex permittivity of the real part of $\varepsilon'$ to more than MnFe$_2$O$_4$. 2-15GHz, MnFe$_2$O$_4$ complex permittivity of the imaginary part of $\varepsilon''$ distribution between 1.0 to 1.5 between 15-18GHz apparent formant; ZnFe$_2$O$_4$ by the complex permittivity of the imaginary part of $\varepsilon''$ value fluctuations the, 3-4GHz, 13-14GHz apparent formant.

3.3 Microwave characteristics

There are two fundamental conditions that must be satisfied to achieve low reflection[6]. First, electromagnetic wave can enter into absorbing materials at the greatest extent (impedance matching characteristic). Second, electromagnetic wave entering into the materials can be almost entirely attenuated (attenuation characteristic). The second condition is more important than the first for ferrite materials [7-9]. According to the second, the attenuation constant can be expressed as:

$$\alpha = \sqrt{2\pi f \times \sqrt{(\mu'_r\varepsilon'_r - \mu'_r\varepsilon'_r) + \sqrt{(\mu'_r\varepsilon'_r - \mu'_r\varepsilon'_r)^2 + (\varepsilon'_r - \mu'_r\varepsilon'_r)^2}}} / c$$

(1)

Where $f$ is the frequency of the EM wave, $\mu'_r$, $\mu'_r$, $\varepsilon'_r$, $\varepsilon'_r$ are the complex permeability and complex permittivity, $c$ is the velocity of light in vacuum.
Figure 4. Attenuation constant of AFe$_2$O$_4$ (A=Ni, Mn, Zn) spinel ferrites.

Figure 4 shows that the variation of the AFe$_2$O$_4$ (A=Ni, Mn, Zn) attenuation constant with the frequency. It can be observed that the NiFe$_2$O$_4$ in the low frequency band (2-8GHz) and high band (over 12GHz) has a good attenuation effect on the electromagnetic wave, and the apparent attenuation peaks appear in 6GHz and 16.5GHz. The attenuation constant of the MnFe$_2$O$_4$ tended to increase with increasing frequency trend between 2-7GHz and the attenuation constant in the 7GHz is essentially unchanged. The attenuation peak of the ZnFe$_2$O$_4$ sample appears between 2-6GHz, the value of the attenuation peak in the high frequency portion is small. So it can be judged CoFe$_2$O$_4$ sample absorbing ability is poor and the band of itself is narrow, which is concentrated in the high frequency band, the absorbing weak point of NiFe$_2$O$_4$ is 8-14GHz, the absorbing properties of the MnFe$_2$O$_4$ is more balanced, the ZnFe$_2$O$_4$ has a strong absorbing ability in high-frequency part.

According to the transmission of electromagnetic wave theory [10-13], when the uniform plane electromagnetic wave injects the bottom layer of the single metal plate absorbing coating vertically, the frequency of which is $f$, the reflectivity power of electromagnetic wave $R$ for the coating is:

$$ R = 20 \log \left| \frac{Z - Z_0}{Z + Z_0} \right| $$

(2)

In the formula, $Z_0$ is the air resistance, $Z$ is the input impedance of materials.

$$ Z = Z_c \tanh(\gamma \cdot d) = Z_0 \sqrt{\mu_r / \varepsilon_r} \cdot \tanh(j 2\pi f \sqrt{\mu_0 \varepsilon_0 \mu_r \varepsilon_r} \cdot d) $$

(3)

where, $\mu_r = \mu_r' - j\mu_r''$ is the relative permeability, $\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$ is Relative dielectric constant, $Z_0 = Z_0 \sqrt{\mu_0 / \varepsilon_0}$ is the characteristic impedance of materials, $\gamma = j 2\pi f \sqrt{\mu_0 \varepsilon_0 \mu_r \varepsilon_r}$ is the propagation constant of electromagnetic wave in the material. $d$ is the thickness of the material.
Substitute the electromagnetic parameters of the ferrite/wax composite into equation (2), the relationship of the doped ferrite analog reflectance and thickness can be calculated from, as shown in Figure 5 the sample absorbing properties is same as the analysis before. It can be obviously seen that the absorbing effect of NiFe$_2$O$_4$ in 2-8GHz and 12-18GHz is better; absorption peaks basically did not move with the change of the thickness; the sample MnFe$_2$O$_4$ matching thickness $\geq$ 3 mm, with the variation of the thickness, its absorption peak moves to the low frequency; ZnFe$_2$O$_4$ sample matching thickness $\geq$ 6mm, the absorption peak is mainly concentrated in the low frequency band (2-6GHz). It can be analyzed from the contour plots of the attenuation constant alpha and reflectivity R, NiFe$_2$O$_4$, MnFe$_2$O$_4$ and ZnFe$_2$O$_4$ complement with each other well in absorbing band. By preparing an appropriate proportion of Ni-Mn-Zn composite spinel ferrite, an excellent absorbing agent will be expected.

4 CONCLUSIONS

In this paper four kinds of typical synthesized spinel ferrites have the high degree of crystallization conditions, complete crystal shape. Due to the different ionic radius and electronegativity of four kinds of ionics (Ni$^{2+}$, Zn$^{2+}$, Mn$^{2+}$), the ion distribution in four kinds of ferrite is different, so that the electromagnetic parameters and absorbing properties changed. The electromagnetic parameters are tested by coaxial method to calculate the contour map of the attenuation constant $\alpha$ and reflectivity R: it can be found NiFe$_2$O$_4$ in the low frequency (2-8GHz) and high frequency (over 12GHz) has good effect on the attenuation of electromagnetic wave, the obvious attenuation peak appears in the 6GHz and 16.5GHz. The attenuation constant of MnFe$_2$O$_4$ in 2-7GHz increase with the increasing of frequency, the attenuation constant remained unchanged after 7GHz. The attenuation peak of ZnFe$_2$O$_4$ samples appears at 2-6GHz, in the high frequency part the attenuation peak is smaller; the absorbing effect of NiFe$_2$O$_4$ in 2-8GHz and 12-18GHz is good; the matching thickness MnFe$_2$O$_4$ samples are 3mm, along with the change in thickness, the absorption peak moves to low frequency; the matching thickness ZnFe$_2$O$_4$ samples are 6mm, The absorption peak is concentrated in low frequency (2-6GHz). It can be judged the absorbing weak point of NiFe$_2$O$_4$ is 8-14GHz, the absorbing performance MnFe$_2$O$_4$ is relatively balanced, as for the ZnFe$_2$O$_4$ it has strong absorbing ability in high frequency part. It can be analyzed from the contour map of reflectivity R and attenuation constants $\alpha$, NiFe$_2$O$_4$, MnFe$_2$O$_4$ and ZnFe$_2$O$_4$ in the
absorption band has a good complementary. By preparing appropriate proportion Ni-Mn-Zn composite spinel ferrite, an excellent wave absorbing agent will be expected.

REFERENCES