

Microstructure and Microwave Absorption Properties of Y-Substituted Ni-Zn Ferrites

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ABSTRACT

The Yttrium ions substituted Ni-Zn ferrites powders were prepared using a sol-gel technique. The crystal structure, magnetic properties and microwave absorption properties of the Ni-Zn ferrites powders were studied by X-ray diffraction, vibrating sample magnetometer and vector network analyzer. The results show that the microwave absorption properties of the Ni-Zn ferrites can be improved effectively with the substitution of Y ions. The minimum reflection loss of the Yttrium ions substituted Ni-Zn powder reaches -34.8 dB, with the -20 dB bandwidth over 2 GHz. The Yttrium substitution can improve microwave absorption properties of Ni-Zn ferrite due to smaller grain dimension and the higher specific magnetization

Keywords: Nick-Zinc Ferrite; Sol-Gel Preparation; Magnetic Properties; Microwave Absorption

1. Introduction

Due to the fast development in information and communication technology, the environmental pollution from non-ionizing microwave irradiation has increased, and there are many researches on various materials which can be used as microwave absorbing and shielding materials. Nickel-zinc ferrites are a well-known class of technologically important ferrite used as microwave absorbing materials [1-3]. Microwave absorption properties are highly dependent on processing parameters and chemical composition. These factors can greatly influence the crystal size, magnetic properties, complex magnetic permeability (μ_r) and complex permittivity (ϵ_r) [4-7]. The Ni-Zn ferrite is a well-known mixed inverse spinel, whose unitary cell is represented by the formula $(Zn_xFe_{1-x})[Ni_{1-x}Fe_{1+x}]O_4$ [8]. The addition of impurities induces changes in the defect structure and texture of the crystal [9], creating significant modifications in the magnetic and electrical properties of these materials. However, the synthesis route also plays a crucial role, so that samples of comparable crystallite size prepared by different processes show different electrical and magnetic properties. There are many methods to synthesize Ni-Zn ferrite, such as co-precipitation [5], thermal plasma [10], hydrolysis [11] etc.

The influences of rare earth (RE) substitution on the

structural and magnetic properties of Ni-Zn ferrites have been studied [12,13]. The partial substitution of Fe^{3+} with a small amount of RE ions increases the electrical resistivity and the relative loss factor, whereas it slightly decreases Curie temperature, and the ferrites were made by the reaction combustion synthesis method and sintered at 1200°C [12]. However, few studies have been done on the microwave absorption properties of these rare earth substitution Ni-Zn ferrites.

According pre-experiment, among different Ni-Zn ratios in the $Ni_xZn_{1-x}Fe_2O_4$, the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ possess of excellent magnetic properties. In this work, the Y-substituted $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrites were prepared by sol-gel followed by a citrate-nitrate auto-combustion process in order to obtain the substitution ferrites at a relatively lower temperature; The influences of Y^{3+} substitution on the microstructure, magnetic properties and microwave absorption properties were investigated. Yttrium was selected as doped element because of its comparable radius with Fe.

2. Experimental

2.1. Synthesis

The $Ni_{0.7}Zn_{0.3}Y_xFe_{2-x}O_4$ ($x = 0, 0.2$) ferrite powders were prepared using sol-gel technique followed by an auto-combustion process. The stoichiometric amounts of $Ni(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$

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were dissolved in deionized water followed by the addition of citric acid. The solution was slowly evaporated at 353 K. The dry gel obtained after dried in 383 K was ignited in air and burned into dendritic and brittle powders. They were finally calcined at 1173K for one hour.

2.2. Characterization

The crystal structure of the materials were determined with X-ray diffraction (XRD) carried out on a Bruker-AXS D8 Advanced diffractometer with Cu K_{α} radiation in the 2θ range from 10 to 80 with steps of 0.02, measurement time 2 s, measurement temperature 25°C, standard: Si powder. The magnetic properties including of specific saturation magnetization (σ_s) and coercivity (H_c) of powders were measured with a vibrating sample magnetometer (VSM) model 155 (made in ED&G PRINCETON APPLIED RESEARCH U.S.A.) at a maximum applied field of 15 KOe at room temperature.

The specimens for microwave absorption test are prepared by mixing the $Ni_{0.7}Zn_{0.3}Y_xFe_{2-x}O_4$ ferrite powders with 30 wt% paraffin wax and made into a toroidal shape (φ_{out} : 7.03 mm, φ_{in} : 3.00 mm). The relative permeability and permittivity values of the specimens were measured in the 2 - 18 GHz using a network analyzer (Agilent Technologies 8722ES). The reflection loss (RL) curves were calculated from the relative permeability and permittivity at the given frequency and absorber thickness, according to the following equations [14]:

$$Z_{in} = Z_0 (\mu_r \varepsilon_r)^{1/2} \tanh \left\{ j(2\pi ft/c)(\mu_r \varepsilon_r)^{1/2} \right\} \quad (1)$$

$$RL(\text{dB}) = 20 \log \left| (Z_{in} - Z_0) / (Z_{in} + Z_0) \right| \quad (2)$$

where f is the frequency of microwave, t is the thickness of absorber, c is the velocity of light, Z_0 is the impedance for free space, and Z_{in} is the input impedance of absorber. The RL values of -20 dB is comparable to the 99% of microwave absorption according to Equations (1) and (2), and thus “RL < -20 dB” is considered as an attractive potential microwave application.

3. Results and Discussions

3.1. Crystal Structure Analysis

For comparison purpose, the XRD patterns of original Ni-Zn ferrite is given in **Figure 1(a)**, and the XRD patterns of Y-substituted Ni-Zn ferrite is shown in **Figure 1(b)**. All the specimens were calcined at 1173K for 1 h in air. The crystal structure of $Ni_{0.7}Zn_{0.3}Y_{0.2}Fe_{1.8}O_4$ determined from **Figure 1(b)** is spinel ferrite; no characteristic peaks for other phases are detected. It can be deduced that the Y are completely doped into the Ni-Zn ferrite. The cell parameters of the ferrites were refined using least square refinement methods. Average crystallite size

(D) of all the samples is calculated using the Debye-scherrer equation [15] given by

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (3)$$

where λ is the wavelength of the X-ray radiation used and β is the full width at half intensity maximum (FWHM) of the most intense peak and θ is the diffraction angle of the most intense peak (311). The results are given in **Table 1**. It can be seen that the change of the lattice parameter after the doping of Y is minor, and the crystallite size of the substituted Ni-Zn ferrites is much smaller. The magnetic properties were also shown in **Table 1**. It can be seen that the specific saturation magnetization (σ_s) increased and the coercivity (H_c) decreased with the substitution of Y. It is thus expected that the substituted-NiZn ferrite might possess different microwave absorbing properties when compared with the NiZn ferrites.

There are two possible existence state of Y in the Ni-Zn ferrites: Some of Y^{3+} entered the lattice and substituted the Fe^{3+} ; other Y diffused to the grain boundary during the sintering process. Y^{3+} ion entering the lattice can result in the increasing of the lattice parameter because of Y^{3+} ion's larger radius (0.73 Å) than Fe^{3+} (0.67 Å); But Y congregating at grain boundary will reduce lattice parameter due to the vacancies left in the Ni-Zn lattice; As a combination of the two effect described above, no significant overall lattice parameter change can be observed. As for the crystallite sizereducing, two kind

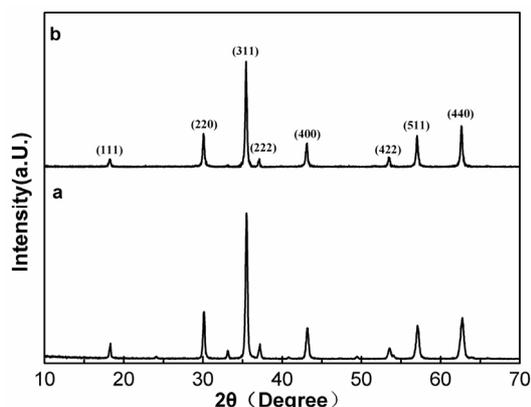


Figure 1. XRD patterns of $Ni_{0.7}Zn_{0.3}Y_xFe_{2-x}O_4$ ferrites ((a) $x = 0$; (b) $x = 0.2$).

Table 1. Lattice parameters, grain sizes and magnetic properties of $Ni_{0.7}Zn_{0.3}Y_xFe_{2-x}O_4$ ferrites.

Substitution amount x	Lattice parameters (Å)	Crystallite size (nm)	Magnetic Properties	
	a		σ_s (emu/g)	H_c (Oe)
0	8.382 ± 0.003	76.4	59.32	130
0.2	8.380 ± 0.002	39.7	64.85	110

of Y existence state both can constrain the growth of the grain: The Y substitution in the lattice will induce lattice distortion, internal stress caused by this distortion hinders the growth of grains; If Y diffused to the grain boundaries, that will also restrain the grain growth by lower down the grain mobility; That explains why the crystallite size of the substituted Ni-Zn ferrite is much smaller than un-doped ferrites. Similar results have also been reported in the literature [12,13].

3.2. Dielectric and Magnetic Parameters

Figure 2(a) shows the real part (ϵ') and the imaginary part (ϵ'') of the relative complex permittivity for ferrites within the frequency of 2 - 18 GHz. It showed that the Y substitution increase the relative permittivity in the GHz frequency range, which is consistent with the result of literature [9]. The probable reason is the substitution induce more electric dipole, so the imaginary part of the relative complex permittivity (ϵ'') increase. The real part (μ') and the imaginary part (μ'') of the relative complex permeability are plotted as a function of frequency in **Figures 2(b)** and **2(c)**. With the substitution of the Y, the μ'' values will increase, it can be explained from the change of the magnetic properties. For the single wall anisotropic particles, there is

$$\mu'' = M_s / 2\mu_0 H_A \alpha \quad (4)$$

$$H_A = 2K_1 / M_s \quad (5)$$

$$\mu_r'' = M_s^2 / 4\mu_0 K_1 \alpha \propto \sigma_s^2 / H_c \propto M_s^2 / H_c \quad (6)$$

where M_s is saturation magnetization, α is Gilbert damping coefficient, μ_0 is permeability of vacuum, H_A is anisotropy field, K_1 is the anisotropy constant. So with the increase of specific saturation magnetization (σ_s) and the decrease of the coercivity, the μ'' values increase.

3.3. Microwave Absorbing Properties.

Figure 3 shows a typical relationship between RL and frequency for the $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ferrite (**Figure 3(a)**) and $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Y}_x\text{Fe}_{2-x}\text{O}_4$ ferrite (**Figure 3(b)**) with the absorber thickness of 1.5 - 3.5 mm. The minimum reflection loss is equivalent to the occurrence of minimal reflection of microwave power. The minimum reflection loss of the $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ferrite was only -24.5 dB at 8.5GHz with a thickness of 2.5 mm (**Figure 3(a)**) However, for Y doped ferrite, the RL values less than -20 dB were recorded in the 6.2 - 8.9 GHz with the absorber thickness of 1.5 - 3.5 mm. In particular, a minimum RL of -34.8 dB was obtained at 8GHz with a thickness of 2.5 mm and its bandwidth less than -20 dB is 2.1 GHz (**Figure 4(b)**). It can be seen that the microwave absorption properties are improved comparing with non-

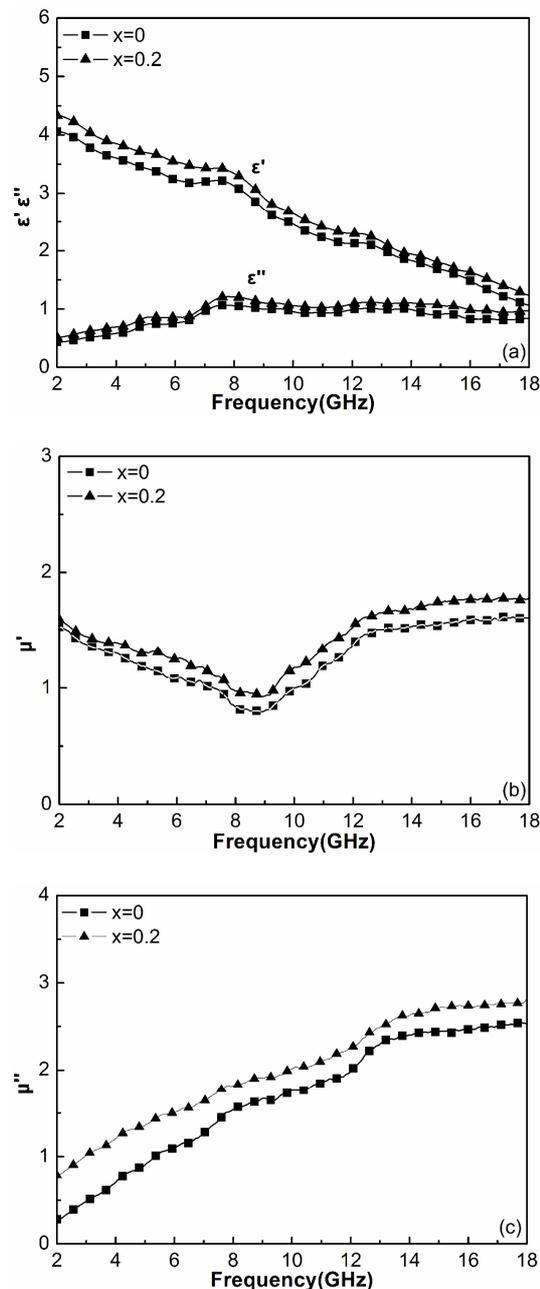


Figure 2. Frequency dependences of relative permittivity ϵ (a), real part μ' (b), and imaginary part μ'' (c) of relative permeability for the Y-substituted ferrites.

substituted ferrites. The frequency at which the RL value reaches minimum moved to lower frequency because of the substituted, which is related to the change of coercivity (H_c).

The improvement of microwave absorbing properties of the ferrites might can be explained as following: Firstly, the substitution made the crystallite sizes smaller and deformed the lattice, which will induce repetitious reflection when the microwave spreading in the ferrites, so more energy will be absorbed; Secondly, the substitu-

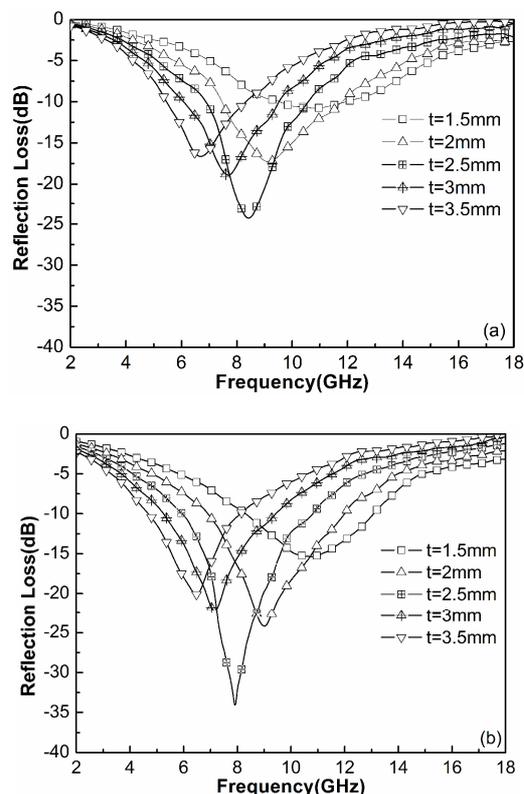


Figure 3. Frequency dependence of RL for $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Y}_x\text{Fe}_{2-x}\text{O}_4$ ferrite ($x = 0$, (a); $x = 0.2$, (b)) at different thickness.

tion can influence the microwave absorption performance by increasing the imaginary part of the relative complex permittivity (ϵ'') and permeability (μ''). So, the Y substituted NiZn ferrite got much better microwave absorption properties.

4. Conclusion

The $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Y}_x\text{Fe}_{2-x}\text{O}_4$ powders were prepared using sol-gel technique. The crystallite size of the $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Y}_{0.2}\text{Fe}_{1.8}\text{O}_4$ is smaller than that of the $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$. The specific saturation magnetization (σ_s) increased and the coercivity (H_c) decreased with the substitution of Y. The imaginary part of permeability and permittivity value of substituted ferrites both increased comparing with that of $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$. The Y substitutions make the minimum reflection loss frequency shift to a lower frequency and the frequency range of RL < -20 dB expand comparing with that of $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ferrite. The improvement of absorption performance may be attributed to the relative permeability and permittivity change and the grain refinement induced by the Y substitution.

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