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The preparation and microwave properties of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ ferrite obtained by a sol–gel process☆

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Abstract

$BaZn_{2-Z}Co_ZFe_{16}O_{27}$ hexaferrites with $Z=0.0,0.6,0.9,1.5$ and 2.0 have been prepared at 1200 °C for 5 h by the citrate sol–gel process. The complex dielectric constant and complex permeability of hexaferrite-paraffin wax composites have been measured by the transmission/reflection coaxial line method in the range from 100 MHz to 6 GHz. Results show that both the complex dielectric constant and dielectric loss exhibit no significant change, with dielectric loss values near to zero in the whole measuring frequency range. It also has been shown that the real part of permeability decreases with the increase of frequency for all samples, whereas the imaginary part increases with the frequency until reaching a peak value, after which it decreases again for samples with $Z=0.0,0.6,0.9$ and 2.0. Substitution of zinc ions substantially affects the microwave properties of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ ferrites.

Keywords: $BaZn_{2-Z}Co_ZFe_{16}O_{27}$; Hexaferrites; Sol–gel; Microwave properties

1. Introduction

Hexagonal ferrites are a wide family of ferromagnetic oxides with peculiar and useful properties. The crystal structure of the different known types of hexagonal ferrites (M, W, X, Y, Z and U) is very complex and can be considered as a superposition of R and S blocks along the hexagonal C axis, RSSR*S*S* for W type, RSRSSR*S*R*S*S* for X type, and RSR*S* for M type, where R is a three-oxygen-layer block with composition $BaFe_6O_{11}$, S (spinel block) is a two-oxygen-layer block with composition Fe_6O_8, and the asterisk means that the corresponding block has been turned 180° around the hexagonal axis. W-type hexaferrite has been extensively studied for its particular magnetic properties. The frequency and temperature dependence of the dielectric constant have been studied in [1–3]. The effects of rare-earth elements on the magnetic properties and microstructure have been investigated in [4]. The relation between magnetic properties and substitutions of various kinds of metal ions has been discussed in [5]. The relaxation of the initial permeability in polycrystalline Ti-doped Ba-W hexaferrites has been measured in [6].

The W-type hexaferrites are usually prepared by the classical ceramic method, i.e. calcination of a mixture of barium carbonate, iron oxide and metal oxide (such as ZnO, CoO, etc.) at high temperature, which results in large aggregates and inhomogeneous compositions. The sol–gel technique provides a means for atomic scale mixing of multiple components at low temperature, which induces a more homogenous precursor, hence improved sintering rates at lower temperatures. In this paper the citrate sol–gel technique has been used to prepare a series of W-type $Ba_2Zn_ZCo_{2-Z}Fe_{16}O_{27}$ hexaferrites with $Z=0.0,0.6,0.9,1.5$ and 2.0. The effects of composition on complex permeability and complex dielectric constants have been investigated, and the frequency dependence of electric constant and permeability in the range from 100 MHz to 6 GHz.

2. Experimental procedure

2.1. Ferrite powder preparation

A series of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ ferrites with $Z=0.0,0.4,0.8,1.2$ and 2.0 were prepared by the sol–gel

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technique. Stoichiometric amounts of ferric citrate and barium carbonate were dissolved together in a minimum amount of citric acid aqueous solution at 80 °C to get a clear solution, then stoichiometric amounts of cobalt nitrate and zinc nitrate were added to the solution. Ammonia solution was added drop by drop to increase the pH to facilitate the formation of a homogeneous solution. Then the solution was slowly evaporated until a highly viscous residue was formed. This was removed immediately to prevent further absorption of water and dried in an oven in the temperature range of 120–140 °C. The citrate precursor was decomposed at 450 °C for 5 h, and subsequently annealed at 1000, 1100 and 1200 °C with a heating rate of 5 °C/min, to obtain $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ crystalline ferrite. A schematic of the preparation process is shown in Fig. 1.

2.2. Microwave measurements

To determine the complex permeability (μ^*) and complex dielectric constant (ε^*) spectra of the $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ ferrite, the powders were randomly dispersed in paraffin wax with volume fraction 25% then die-pressed to form cylindrical toroidal samples with 3.0 mm inner diameter, 7.0 mm outer diameter, and 2–4 mm thickness.

The transmission/reflection coaxial line method was used to measure the microwave complex permeability and permittivity of the ferrite-wax mixture samples. A gold-plated coaxial airline with 7.0 mm connector precision interface was used to hold the samples. An HP8753E vector network analyzer was used to measure the transmission and reflection coefficients of the samples in the frequency range 0.1∼6.0 GHz. The relative complex permeability and permittivity of the samples were calculated from the measured transmission and reflection coefficients with the theoretical formulas described by in [7].

2.3. Structure characterization

The phase structure of the powders fired at 1000, 1100 and 1200 °C for 5 h was investigated by X-ray diffractometry. The precursor powders preheated at 450 °C for 5 h were pressed into 10 mm diameter, 3 mm thick disc-shaped samples under a pressure of 10 kPa. Then the disc-shaped samples were sintered at 1200 °C for 5 h and slowly cooled to room temperature. Finally the samples were ground, polished and etched by HF acid, and their microstructure observed by scanning electron microscopy (SEM).

3. Results and discussion

Fig. 2 gives the XRD patterns of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ with $Z=0.9$ synthesized by the citrate sol–gel route and heat-treated at 1000, 1100 and 1200 °C for 5 h. Pure W-type or M-type hexaferrites exist in the sample when the precursor is calcined at 1200 or 1000 °C for 5 h, whereas a W-type and M-type hexaferrite mixture is found as the precursor is annealed at 1100 °C for 5 h. The results also show that the synthesis temperature of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ ferrite of about 1100 °C for the present sol–gel process is much lower than for the classical ceramic method.

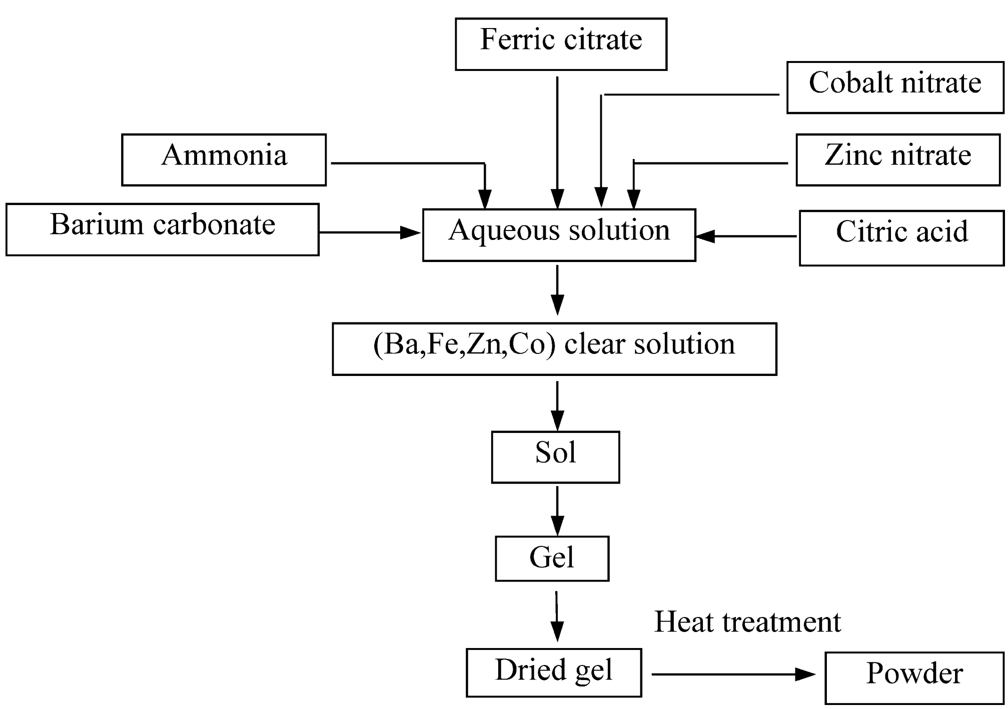

Fig. 1. Schematic diagram of the preparation of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ powder.

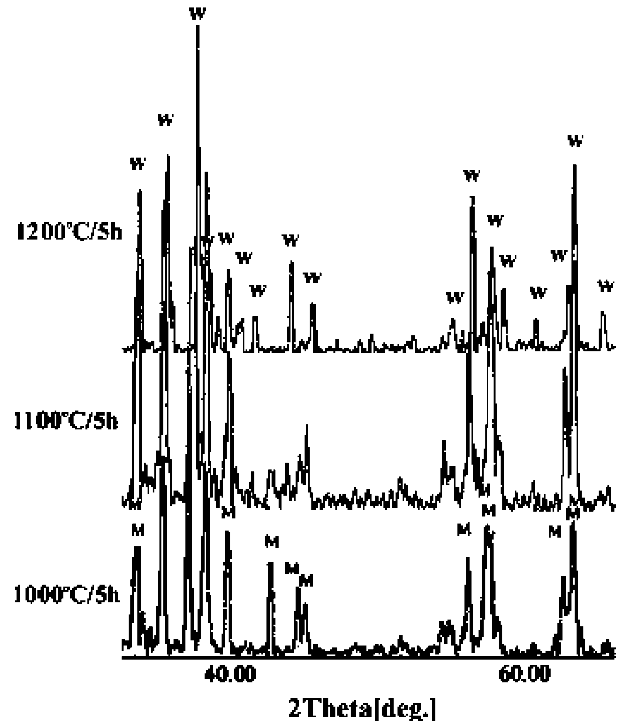

Fig. 2. X-ray diffraction pattern of the precursors heated at 1200 °C for 5 h ($Z = 0.9$).

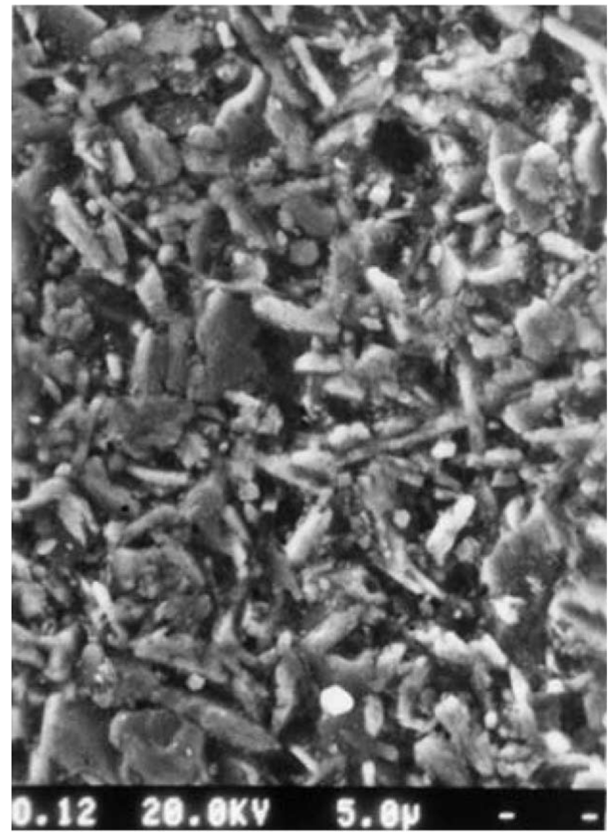

Fig. 3. SEM photograph of the eroded surface of $BaZn_{2-Z}Co_Z Fe_{16}O_{27}$ sintered at 1200 °C for 5 h.

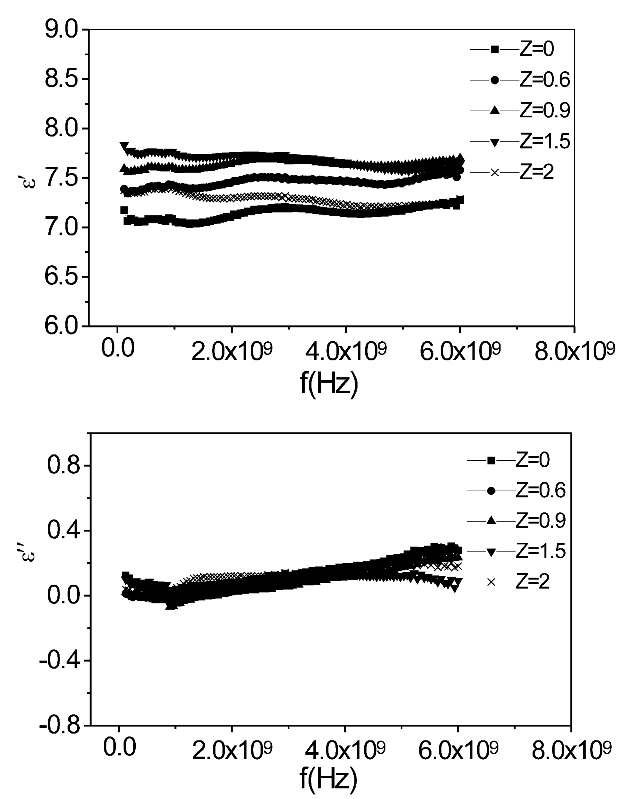

Fig. 4. Frequency dependence of ε′ and ε′ of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ (1200 °C/5 h) ferrite-wax composite.

Fig. 3 shows the microstructure of an eroded surface of $BaZn_{1.1}Co_{0.9}Fe_{16}O_{27}$ ferrite calcined at 1200 °C for 5 h in air. Laminar grains with size of about 1.0 by 5.0 μm on average can be observed.

Fig. 4 shows the variation of the complex dielectric constant ε^* with frequency for all $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ ferrite samples calcined at 1200 °C in the frequency range from 100 MHz to 6 GHz. It indicates that all samples with $Z = 0,0.6,0.9,1.5$ and 2.0 exhibit no significant variation of ε' and ε'' in the range from 100 MHz to 6 GHz. It is also found that the composition dependent ε' values show a maximum for the sample with $Z = 1.5$ and a minimum for the sample with $Z = 2.0$.

Fig. 5 illustrates the frequency dependence of the real and imaginary parts of permeability for all samples in the range from 0.1 to 6.0 GHz. μ' Decreases monotonically with frequency and this decrease is more rapid at low frequency than at high frequency. μ'' rises with frequency until it reaches a maximum value after which it decreases again for samples with $Z = 0.0,0.6,0.9$ and 2.0. The peak value of μ'' is the result of natural resonance phenomena, the natural resonance frequency shifting toward lower frequency with increasing Zinc ion content (for Zn_2W, $f_{res} = 600$ MHz, for $Zn_{1.4}Co_{0.6}W$, $f_{res} = 840$ MHz, for $Zn_{1.1}Co_{0.9}W$, $f_{res} = 1.08$ GHz, for Co_2W, $f_{res} = 1.26$ GHz). However, the imaginary part of permeability of $Zn_{1.5}Co_{0.5}W$ hexaferrite rises with frequency in the range from 0.1 to 6.0 GHz and no resonance phenomena can be observed in the curve of μ'' versus f. Further investigation is needed to clarify this aspect.

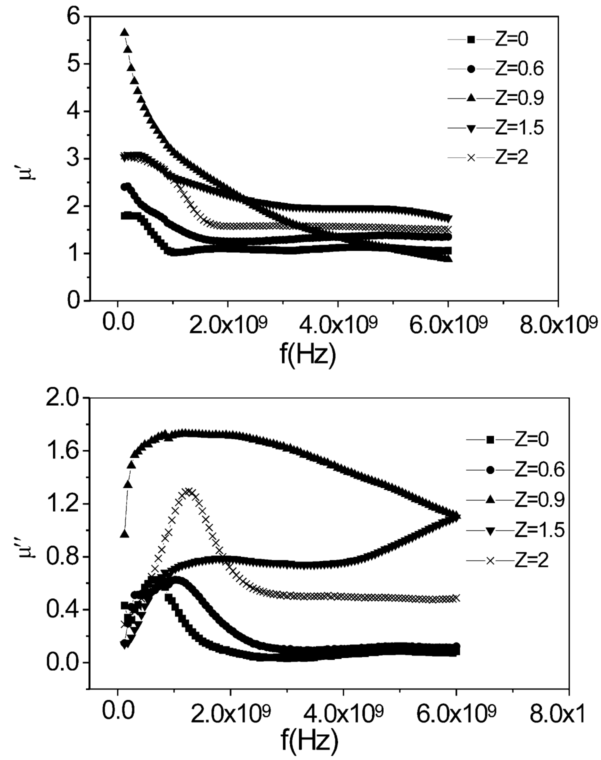

Fig. 5. Frequency dependence of μ' and μ'' of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ (1200 °C/5 h) ferrite-wax composite.

In the materials with planar anisotropy, the natural FMR frequency will be determined by the rotational stiffness of the magnetization within the preferred plane as well as by that out of the preferred plane. The resonance condition is given by,

$$2\pi f_{\text{res}} = \gamma\sqrt{H_\theta H_\phi} \tag{1}$$

where H_ϕ and H_θ are the corresponding anisotropy fields. H_θ is connected with the crystal anisotropy constants K_1 and K_2 while usually have high value; H_ϕ is connected with the crystal anisotropy constant K_3, which is a measure of the stiffness of the rotation in the preferred plane. The anisotropy field of W hexaferrite becomes smaller as the zinc content increase, thus the natural FMR resonance frequency of these ferrite decreases with the increase of zinc content.

Fig. 6 shows the frequency dependence of dielectric loss and magnetic loss in the range of 0.1–6 GHz for all samples. It shows that the dielectric loss is very small at all frequencies and that the magnetic loss increases with frequency for $Zn_{1.1}Co_{0.9}W$ and $Zn_{1.5}Co_{0.5}W$ hexaferrite in the range of 0.1–6 GHz. However, for samples Zn_2W, $Zn_{1.4}Co_{0.6}W$ and Co_2W, magnetic loss increases with frequency at lower frequencies until it reaches a peak at about 800 MHz$\sim$1.5 GHz, subsequently μ''/μ' decreases with frequency at first, then keeps constant at high frequencies.

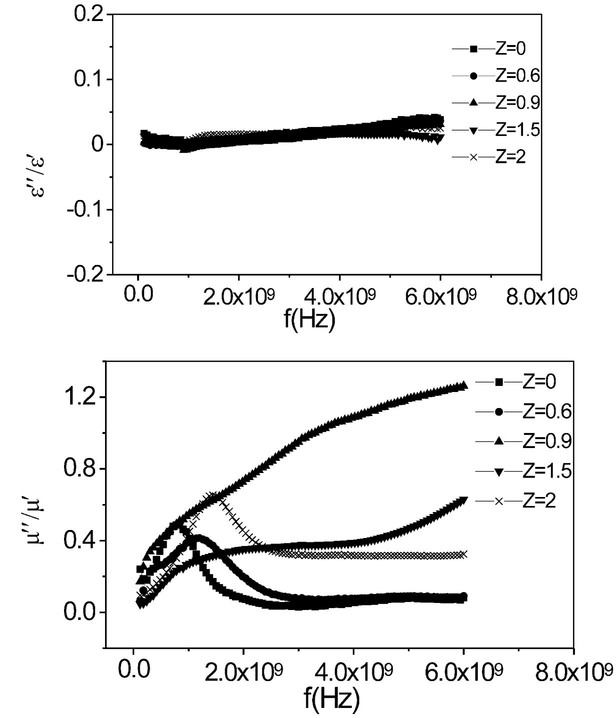

Fig. 6. Frequency dependence of dielectric and magnetic loss of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ (1200 °C/5 h)ferrite-wax composite.

According to the transmission line theory, the reflection coefficient (dB) is a function of the normalized input impedance at the surface of a single layer material backed by a perfect conductor, which is expressed as follows,

$$R = 20\ \lg|\Gamma| = 20\ \lg\left|\frac{Z_{\text{in}}(N) - Z_0}{Z_{\text{in}}(N) + Z_0}\right| \tag{2}$$

where Z_0 is the characteristic impedance of free space,

$$Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}} \tag{3}$$

Z_{in} is the input impedance at free space and material interface,

$$Z_{\text{in}} = \sqrt{\frac{\mu_0\mu^*}{\varepsilon_0\varepsilon^*}}\tanh\left(j2\pi f\sqrt{\mu_0\mu^*\varepsilon_0\varepsilon^* d}\right) \tag{4}$$

where f and d are the frequency of electromagnetic wave and the thickness of the material, respectively. The reflection coefficients can be calculated by using Eqs. (2)–(4). Obviously, the reflection coefficient is negative, and the lower the reflection coefficient, the higher the absorption. The calculated microwave reflection coefficients of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ hexaferrite with $d = 3$ mm in the frequency range from 0.1 to 6 GHz are shown in Fig. 7. It can be seen that reflection loss increases with frequency for all the samples, the maximum reflection loss being about 20 dB at 6 GHz for the $Z = 1.5$ sample.

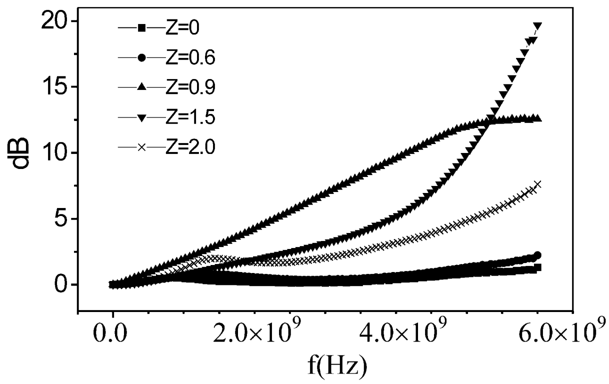

Fig. 7. The calculated reflection loss of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ (1200 °C/5 h) ferrite-wax composite.

4. Conclusions

$BaZn_{2-Z}Co_ZFe_{16}O_{27}$ hexaferrites were prepared by the citrate sol–gel technique at 1200 °C for 5 h using ferric citrate, barium carbonate and metal nitrates precursors. The complex permittivity and complex permeability spectra of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ hexaferrites in the frequency range 0.1–6 GHz were measured. It was found that the complex permittivity exhibits no significant variation in the whole measuring frequency, whereas Zinc ion content affects the natural resonance frequency of $BaZn_{2-Z}Co_ZFe_{16}O_{27}$ ferrites, which shifts towards lower frequency with the increase of zinc ion content.

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