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The preparation and microwave properties of $Ba_2Zn_zCo_{2-z}Fe_{12}O_{22}$ hexaferrites

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Abstract

$Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ hexaferrites with $Z = 0.0$, 0.4, 1.2, 1.6 and 2.0 were prepared at temperature 1100 °C for 5 h by citrate sol-gel process. The complex dielectric constant and complex permeability of hexaferrite–paraffin wax composites had been measured by the transmission/reflection coaxial line method in the range from 100 MHz to 6 GHz. The results show that both the complex dielectric constant and dielectric loss decrease as measuring frequency increases, the dielectric loss were near to zero at high frequency. It also shows that the real part of permeability decreases as the frequency increases in the whole range of measuring frequency. The natural phenomenon is observed in μ'' spectrum for $Zn_{0.4}Co_{1.6}Y$, $Zn_{1.2}Co_{0.8}Y$, $Zn_{1.6}Co_{0.4}Y$ and Zn_2Y hexaferrites. The substitution of Zinc ions had a close effect on the microwave properties of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ ferrites, the higher the Zinc ions content, the lower the natural resonance frequency is. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: $Ba_2(Zn,Co)_2Fe_{12}O_{22}$; Ferrites; Hexaferrites; Microwave properties; Sol-gel processes

1. Introduction

Hexaferrites are classified into five main types depending on chemical formula and crystal structure. These are the M-type ($BaFe_{12}O_{19}$), W-type ($BaMe_2Fe_{16}O_{27}$), Y-type ($Ba_2Me_2Fe_{12}O_{22}$), Z-type ($Ba_3Me_2Fe_{24}O_{41}$) and X-type ($Ba_2Me_2Fe_{28}O_{46}$). Among them, Y-type ferrite is constructed from basic units of hexagonal barium M ferrite and cubic spinel ferrites, which retain a hexagonal structure, usually with the direction of magnetization parallel to the *c*-axis. However, if the metal M = Cobalt II, or Zinc II, then Co_2Y, Zn_2Y are formed, known as ferroxplana ferrites, so called because they possess an easy plane (basal plane) of magnetization perpendicular to the *c*-axis.[1,2] This results in a reduction of applied magnetic field required for ferromagnetic resonance and thus provides an ideal material for use at GHz frequency. The spinel ferrites can be only used up to 300 MHz.[3] Because of this, the ferroxplana ferrites are commercially important materials to be used for inductor cores, u.h.f. communications and other high frequency applications.[4] The magnetic permeability has been studied for the Y-type hexaferrites $Ba_2Ni_{2-x}Zn_xFe_{12}O_{22}$[5,6] while the ferromagnetic resonance linewidths in single crystals of Mn-doped $Ba_2Zn_2Fe_{12}O_{22}$ has been measured as a function of frequency (0.01–40 GHz) and temperature (4–300 K).[7]

The classical ceramics method for preparing $Ba_2Me_2Fe_{12}O_{22}$[8,9] ferrite requires a high calcining temperature, which induces aggregation of the particles. Afterwards, the milling process generally yields nonhomogeneous mixtures on a microscopic scale and introduces lattice strains in the materials. To achieve homogeneity of ions at atomic level in the precursor, the sol-gel technique is used for preparing a series of Y-type $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ hexaferrites with more perfect crystallography. Moreover, a narrow size distribution has been achieved in this paper. The effect of composition on complex permeability and complex dielectric constants and their dependences on frequency have been studied.

2. Experimental procedure

2.1. Preparation of hexaferrite powder

A series of ferrite samples of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ with $Z = 0.0$, 0.4, 1.2, 1.6 and 2.0 were prepared by using

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a citrate sol-gel technique. A stoichiometric amount of ferric citrate and barium carbonate was dissolved in a citric acid aqueous solution at 80 °C, and then a stoichiometric amount of cobalt nitrate and zinc nitrate was added, yielding a completely homogenous transparent solution within a few seconds. These solutions were slowly evaporated until a highly viscous residue was formed. A dried gel was developed by heating the residue in the temperature range of 120–140 °C. The dried gel was first preheated at 450 °C for 5 h. Then the obtained amorphous precursor was thermally processed to attain $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ ferrite crystalline by the heat-treatment at 1000, 1100 and 1200 °C for 5 h, respectively, using a heating rate of 5 °C/min. A schematic of the preparation process is shown in Fig. 1.

2.2. Preparation of samples

The complex permeability (μ^*) and complex dielectric constant (ε^*) spectrum of the $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ hexaferrite powders were measured using the following technique. The ferrite powders were randomly dispersed in paraffin wax with volume fraction 25%. The ferrite powder and wax mixtures were die-pressed to form cylindrical toroidal specimens with 3.0 mm inner diameter, 7.0 mm outer diameter, and 2–4 mm thick.

2.3. Microwave measurements

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 a connector interface of 7 mm in precision was used to hold the samples to be measured. An HP8753E vector network analyzer was used to measure the transmission and reflection coefficients of the samples over the frequency range of 0.1–6.0 GHz. The relative complex permeability and permittivity of the samples were calculated from the measured transmission and reflection coefficients using the theoretical formulas described by Weir.[10]

2.4. Structure characterization

The powders fired at 1000, 1100 and 1200 °C for 5 h were investigated by means of X-ray diffractometer, using Fe K_α radiation, to characterize the phase structure. The microstructure was observed using scanning electronic microscopy (SEM). For this purpose the precursor powders preheated at 450 °C for 5 h were pressed into disc-shaped samples with diameter 10 mm and thick 3 mm 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.

3. Results and discussion

The XRD patterns of $Ba_2Zn_{1.2}Co_{0.8}Fe_{12}O_{22}$ Y-type hexaferrite samples synthesized by the citrate sol-gel route are shown in Fig. 2. The standard diffraction data

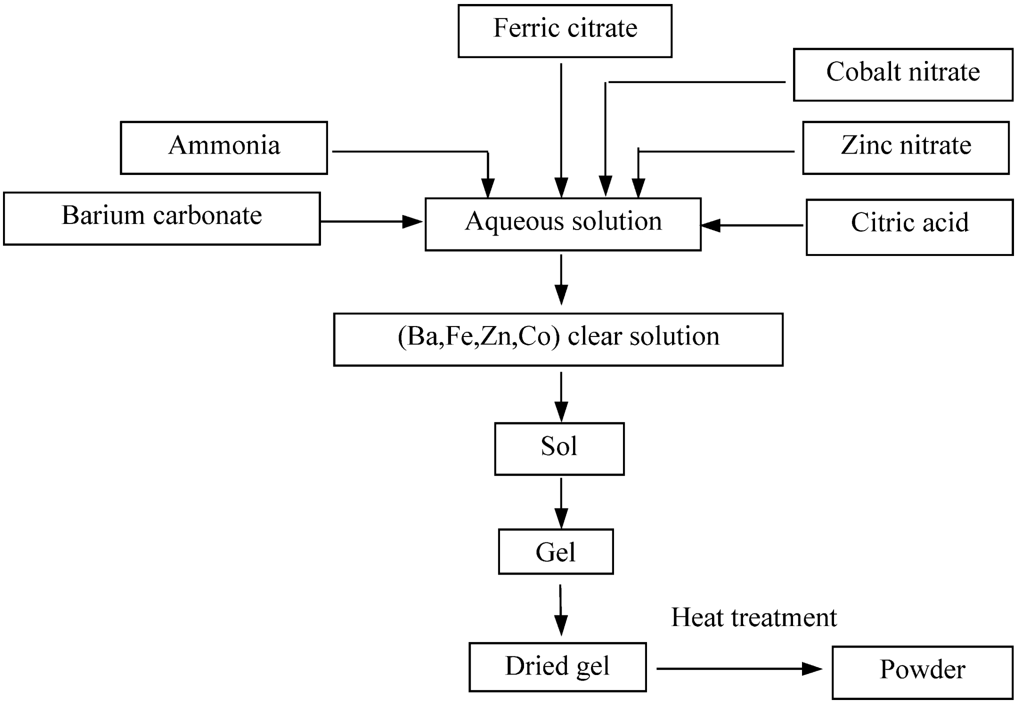

Fig. 1. Schematic diagram of the preparation of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ powder.

of pure M, Y-type (Zn_2Y) hexaferrites and the XRD results of samples annealed at 1100 and 1200 °C with 2θ from 0 to 70° are shown in Table 1. Which results show that Y-type phases and few of M-type hexaferrite are present in the sample when precusor is calcined at 1000 °C for 5 h. As the firing temperature is increased to 1100 and 1200 °C, the only crystalline phase detected by XRD is Y-type hexaferrite. The temperature applied is much lower than that of classical ceramics method to synthesize $Ba_2Zn_{1.2}Co_{0.8}Fe_{12}O_{22}$ ferrite.

The microstructure of eroded surface of $Ba_2Zn_{1.2}Co_{0.8}Fe_{12}O_{22}$ ferrite calcined at 1200 °C for 5 h in air is shown in Fig. 3. It indicates that the Y-type hexaferrite particles fired at 1200 °C are homogeneous hexagonal column-shaped crystals, with an even size of 1.0 by 5.0 μm, also in a narrow distribution.

Fig. 4 shows the variation of complex dielectric constant ε^* with frequency for all $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ ferrite samples ($Z=0.0$, 0.4, 1.2, 1.6 and 2.0) heat-treated at 1200 °C for 5 h and measured by the transmission/reflection coaxial line method. The general behavior of ε' and ε'' with frequency can be summarized as follows. At low frequencies the values of ε' and ε'' are high, and then they decrease with increasing frequencies, finally becoming unchangeable at 6 GHz. It is also found that the values of ε' and ε'' depend on composition, with a maximum value for the hexaferrite samples with $Z=1.2$.

Fig. 5 illustrates the frequency dependence of the real part and imaginary part of permeability for all samples in the range 0.1–6.0 GHz. It can be observed that the real part of permeability (μ') decreases monotonically with increase of frequency for samples with $Z=0.0$, 0.4, 1.2, 1.6 and 2.0, however, this decrease is more rapidly at low frequencies than at high frequencies. It also can be noticed that there is a very obvious resonance phenomenon in FMR spectrum, corresponding to natural resonance, for $Zn_{2.0}Y$ ($f_r=489$ MHz), $Zn_{1.6}Co_{0.4}Y$ ($f_r=848$ MHz) and $Zn_{1.2}Co_{0.8}Y$ ($f_r=1.32$ GHz) hexaferrites, with a very small resonance peak at 3.36 GHz for $Zn_{0.4}Co_{1.6}Y$ hexaferrite. However, no resonance phenomenon can be observed in the FMR spectrum curve for Co_2Y hexaferrite, i.e. the natural resonance peak may appear at higher frequencies beyond measuring range. It also shows that natural resonance frequency has a close relation with Zinc ion content. The resonance peak is shifted toward lower frequencies (from over 6 GHz to

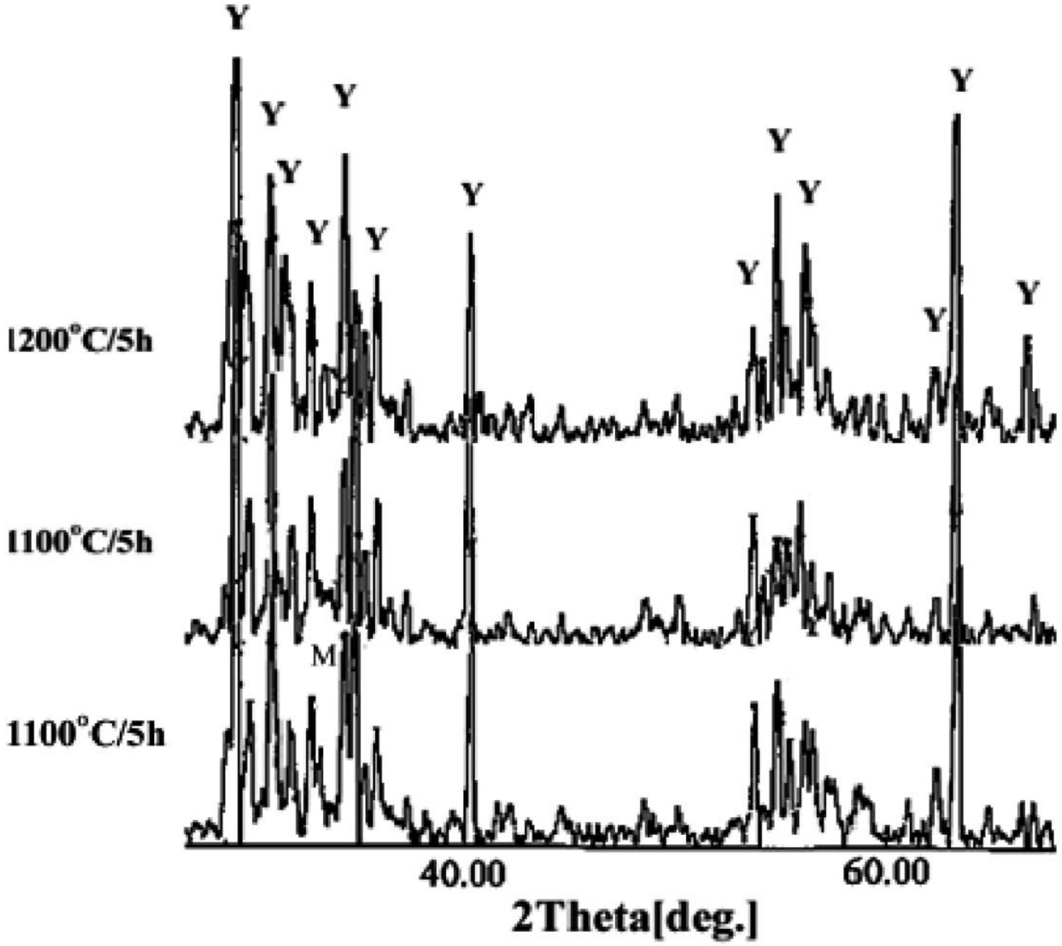

Fig. 2. X-ray diffraction pattern of Y-type hexaferrite $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ powders heated at 1000, 1100, and 1200 °C for 5 h ($Z=1.2$).

Table 1
The standard diffraction data of pure M, Y-type hexaferrites and the XRD results of samples annealed at 1100 and 1200 °C with 2θ from 0 to 70°

M-type JCPDS 43-0002		Y-type JCPDS 44-0207		Sample powder annealed at 1100 °C		Sample powder annealed at 1200 °C	
d Value	Int.	*d* Value	Int.	*d* Value	Int.	*d* Value	Int.
2.9460	45	2.9378	100	2.9398	100	2.9417	100
2.8978	15	2.8787	28	2.8824	36	2.9006	42
2.8552	9	2.8013	81	2.7962	65	2.7980	67
2.7779	89	2.7249	29	2.7217	30	2.7461	39
2.6262	100	2.6558	45	2.6528	35	2.6543	35
2.5513	9	2.5391	10	2.5433	25		
2.5359	5	2.5115	77	2.5116	67	2.5333	65
2.5198	7	2.4793	22	2.4780	22	2.4794	22
2.4227	47	2.4428	26	2.4416	36	2.4429	36
2.2352	30	2.1974	63	2.1974	59	2.1974	53
2.1290	19	1.6966	17	1.6990	31	1.6990	25
1.6666	37	1.6681	25	1.6659	25	1.6857	17
1.6320	21	1.6548	15	1.6532	24	1.6565	25
1.6248	43	1.6364	21	1.6370	35	1.6327	37
1.4730	44	1.4692	44	1.4705	55	1.4692	54

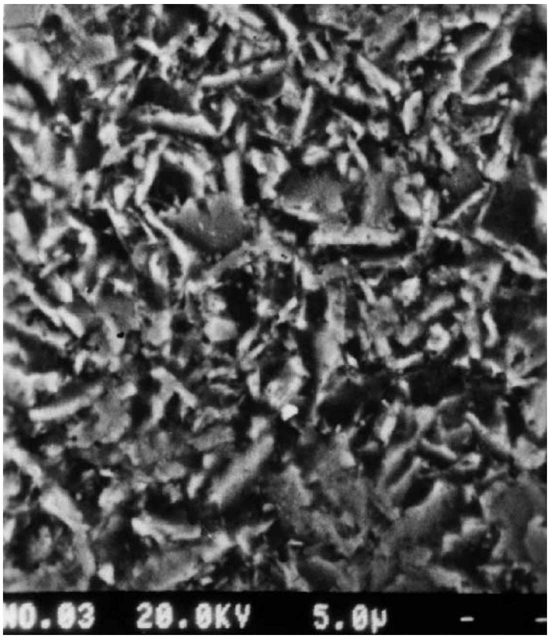

Fig. 3. SEM photograph of the eroded surface of $Ba_2Zn_{1.2}Co_{0.8}Fe_{12}O_{22}$ sintered at 1200 °C for 5 h.

489 MHz) as Zinc ions content is increased from $Z=0.0$ to $Z=2.0$.

In 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 the rotational stiffness of the magnetization out of the preferred plane. The resonance condition is given by,

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

where H_ϕ and H_θ are the corresponding anisotropy fields, respectively. H_θ is connected with crystal anisotropy constant K_1, K_2 which have very high values; 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. If K_3 is small, then H_ϕ can be determined by stress anisotropy and shape anisotropy. The anisotropy field H_ϕ is usually 1000 times smaller than

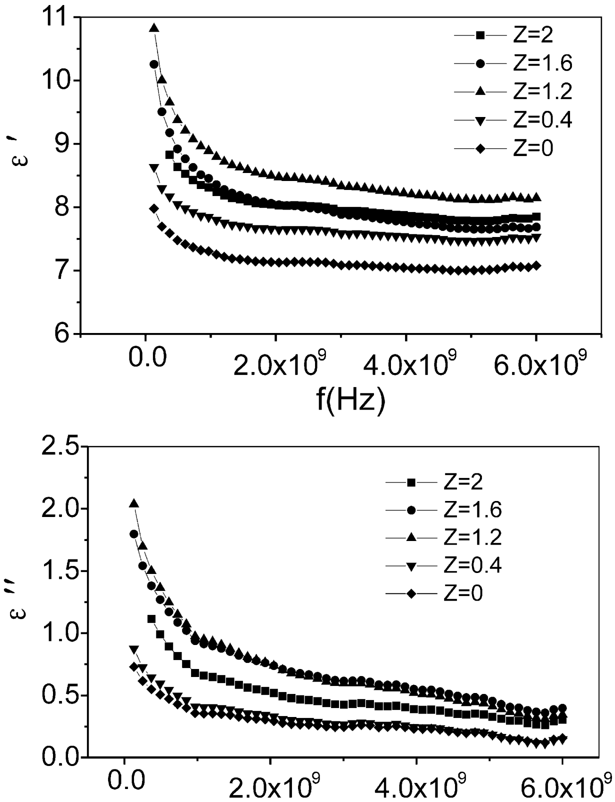

Fig. 4. Frequency dependence of ε' and ε'' of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ (1200 °C/5 h)–wax composite.

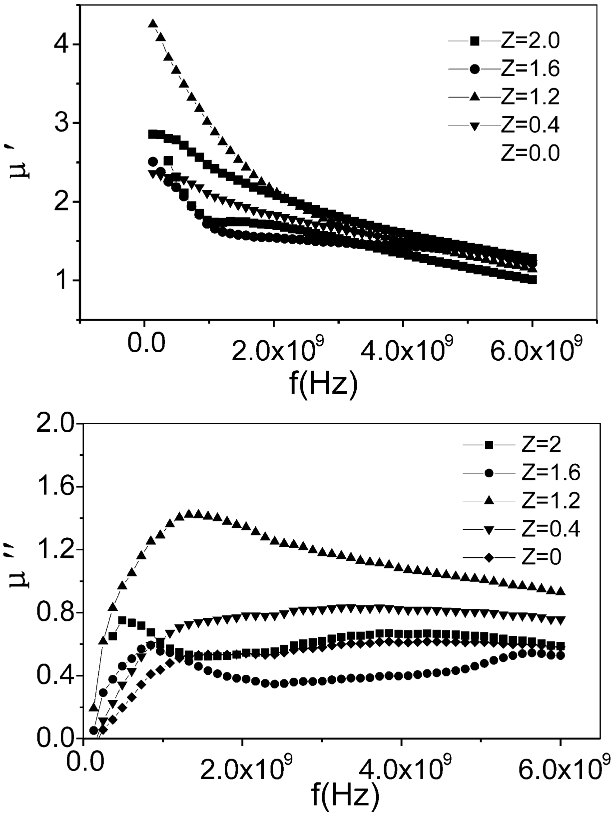

Fig. 5. Frequency dependence of μ' and μ'' of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ (1200 °C/5 h)–wax composite.

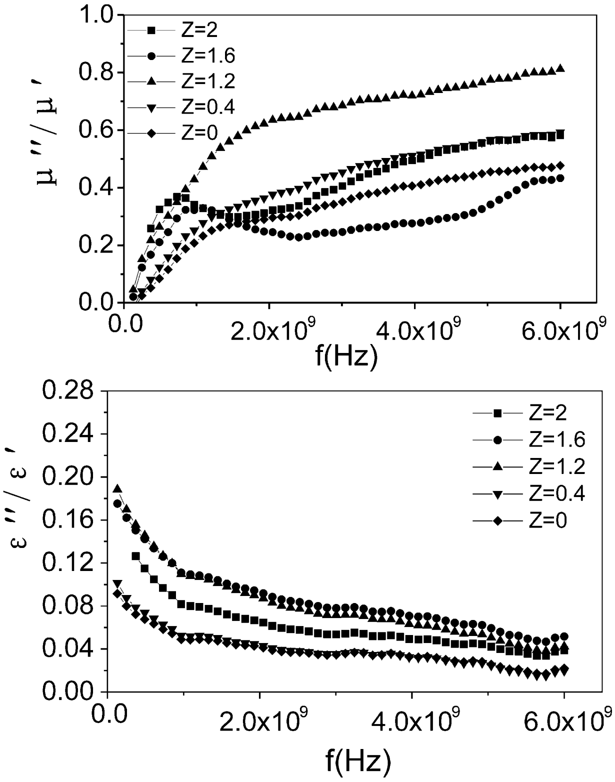

Fig. 6. Frequency dependence of dielectric and magnetic loss of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ (1200 °C/5 h)–wax composite.

H_θ. Assuming that μ_0 is due solely to rotations, H_ϕ will be related to μ_0 according to Eq. (2),

$$\frac{(\mu_0 - 1)}{4\pi} \cong \frac{M_S}{3H_\phi} \tag{2}$$

where μ_0 is the static initial permeability and M_S is the saturation magnetization. Literature values for H_ϕ and H_θ will give an indication of FMR frequency expected for Y hexaferrite studied here. Typically, H_θ is much larger than H_ϕ for Co_2Y, $H_\theta = 2.2\times10^6$ Am^{-1} [1] and $H_\phi \approx 2.71\times10^4$ Am^{-1} [1] resulting in $f_{res} = 8.65$ GHz according to Eq. (1). For Zn_2Y hexaferrite, $H_\theta = 7.166\times10^6$ Am^{-1}, H_ϕ can be estimated from Eq. (2) and is about 845 Am^{-1}, which results in $f_{res} = 487$ MHz by Eq. (1). It is in well agreement with the measurement results. The anisotropy of Y-type hexaferrite becomes smaller as the zinc content increases, thus natural FMR resonance of these ferrite decreases with increase of zinc ions content.

Fig. 6 shows the frequency dependence of dielectric loss and magnetic loss in the range of 0.1–6 GHz for all samples. The dielectric loss is very small and decreases with frequency. The decrease is more rapid at low frequencies than at high frequencies. The maximum value of $\varepsilon''/\varepsilon'$ is observed in dielectric constant spectrum of $Zn_{1.6}Co_{0.4}Y$. It also illustrates that the magnetic loss almost increases with frequency monotonically in the measuring frequency range for all samples but $Zn_{1.6}Co_{0.4}Y$ and Zn_2Y hexaferrite. However, for the latter two samples the magnetic loss increases with frequency in the beginning, until reaching a small peak at about 800–1000 MHz, after which μ''/μ' decreases a little at first, and then increases with frequency.

According to 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 shown below,

$$R = 20\lg|\Gamma| = 20\lg\left|\frac{Z_{in}(N) - Z_0}{Z_{in}(N) + Z_0}\right| \tag{3}$$

where Z_0 is the characteristic impedance of free space,

$$Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}} \tag{4}$$

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

$$Z_{in} = \sqrt{\frac{\mu_0\mu}{\varepsilon_0\varepsilon}}\tanh\left(j2\pi f\sqrt{\mu_0\mu\varepsilon_0\varepsilon}d\right) \tag{5}$$

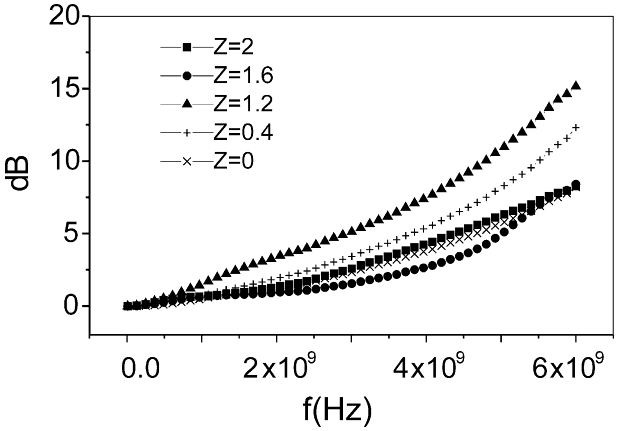

Fig. 7. The calculated reflection loss of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ (1200 °C/5 h)–wax composite.

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. (3)–(5). Obviously, the reflection coefficient is negative, and the lower the reflection coefficient, the higher the absorption is. The calculated microwave reflection coefficients of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ 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 of the samples, and there is a maximum reflection loss for $Zn_{1.2}Co_{0.8}Y$ hexaferrite at 6 GHz, which is about 15 dB.

4. Conclusions

A series of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ hexaferrite are prepared by citrate sol-gel technique at the temperature 1100 °C for 5 h with precursors of ferric citrate, barium carbonate and metal nitrates. The Y-type hexaferrite particles fired at 1200 °C are column-shaped, with an even size of 1.0 by 5.0 μm. The complex permittivity and complex permeability spectrum of all samples have been measured by using transmission/reflection coaxial line method. The results in the frequency range from 0.1 to 6 GHz show that the complex permittivity decreases with increase of frequency; the higher the Zinc ions content, and the smaller the permittivity is. It is also found that Zinc ions content strongly affects the natural resonance frequency of $Ba_2Zn_ZCo_{2-Z}Fe_{12}O_{22}$ hexaferrite. The resonance frequency shifts towards lower frequency from over 6 GHz to 489 MHz as the Zinc ions content increases from $Z=0.0$ to $Z=2.0$.

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References

1. Smit, J. and Wijn, H. P. J., *Ferrites*. Cleaver-Hume Press, London, 1959 (Chapter 9)..
2. Wohlfarth, E. P., *Ferromagnetic Materials*. North-holland, Amsterdam, New York, Oxford, 1982 pp. 305–440..
3. Pullar, R. C., Appleton, S. G. and Bhattacharya, A. K., The microwave properties of aligned hexagonal ferrite fibers. *J. Mater. Sci. Lett.*, 1998, **17**, 973–975.
4. Heck, C., *Magnetic Materials and Their Applications*. Butterworths, London, 1974 pp. 511–517..
5. Kown, H. J., Shin, J. Y. and Oh, J. H., The microwave absorbing and resonance phenomena of Y-type hexagonal ferrite microwave absorbers. *J. Appl. Phys.*, 1994, **75**, 6109–6111.
6. Elata, A. M. A., Ahmed, M. A. and Elhiti, M. A., Physical properties of $Ba_2Ni_{2\text{-}x}Fe_{12}O_{22}$ hexaferrites. *J. Mater Sci. Lett.*, 1999, **18**, 563–567.
7. Dorsey, P., Sun, K., Vittoria, C., Wittenauer, M. A., Friedlander, F. J. and Schindler, A., Ferrimagnetic resonance linewidth in single-crystal Mn-doped $Ba_2Zn_2Fe_{12}O_{22}$. *J. Appl. Phys.*, 1990, **67**, 5524–5526.
8. Shin, J. Y. and Oh, J. H., The microwave absorbing phenomena of ferrite microwave absorbers. *IEEE Trans. Magn. Mag*, 1993, **29**, 3437–3439.
9. Chen, I.-G., Hsu, S.-H. and Chang, Y. H., Preparation and magnetic properties of Ba–Co_2Z and Sr–Zn_2Y ferrites. *J. Appl. Phys.*, 2000, **87**, 6247–6249.
10. Weir, W. B., Automatic measurement of complex dielectric constant and permeability at microwave frequencies, 1974. *Proceedings of the IEEE*, 1974, **62**, 33–36.