

Complex permittivity, permeability, and microwave absorption of Zn- and Ti-substituted barium ferrite by citrate sol–gel process

Zhang Haijun^{a,*}, Liu Zhichao^b, Ma Chengliang^a, Yao Xi^c, Zhang Liangying^c,
Wu Mingzhong^c

^a High Temperature Ceramics Institute, Zhengzhou University, 75, Daxue Road, Zhengzhou Henan Province 450052, PR China

^b Department of Mechanical Engineering, Jiaozuo Institute of Technology, Jiaozuo Henan Province 454100, PR China

^c Functional Materials Research Laboratory, Tongji University, Shanghai 200092, PR China

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Abstract

Ba(ZnTi)_xFe_{12–2x}O₁₉ (*x* varies from 0.2 to 1.0 in steps of 0.2) hexaferrites were prepared by citrate sol–gel process, the formation temperature is about 800 °C. The samples were characterized by XRD, scanning electron microscopy. The effect of Zn²⁺+Ti⁴⁺ substitution, annealing temperature on complex permeability, permittivity and microwave absorption had been studied for Ba(ZnTi)_xFe_{12–2x}O₁₉ ferrite in the frequency range from 100 MHz to 6.0 GHz. All the ferrites exhibit significant dispersion in complex permeability. The dispersion in complex dielectric constant is not significant. The variations of reflection loss have been studied as a function of frequency, Zn²⁺+Ti⁴⁺ content, and thickness of the absorber.

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1. Introduction

Barium ferrite BaFe₁₂O₁₉ is one of the most important hard magnetic materials, widely used for permanent magnets, magnetic recording media and microwave absorbers. For its high stability, excellent high-frequency response and narrow switching field distribution, BaFe₁₂O₁₉ has been studied extensively during the last few years [1–7]. Barium ferrite is a ferromagnetic material, which has a collinear five-sublattice magnetic structure and uniaxial magnetocrystalline anisotropy with easy axis parallel to the *c* axis of the hexagonal unit cell. Its crystal structure can be divided in several blocks according to the stacking form of closely packed oxygen ions. The S block contains two oxygen layers forming a spinel structure and R block is a three-oxygen-layer block, containing the barium ion. A large amount of works have been done to modify the

magnetic parameters of barium hexaferrite by substitution of Fe³⁺ with other cations or cation combinations such as Co–Ti, Zn–Ti, Zn–Sn, Co–Sn, Ni–Zr, Co–Mo and so on [8–12]. The present work investigates the variations of complex dielectric, complex permeability and reflection loss with annealing temperature and substitution of Zn²⁺+Ti⁴⁺ ions in BaFe₁₂O₁₉ hexaferrites.

2. Experimental procedure

The hexaferrites with composition Ba(ZnTi)_x-Fe_{12–2x}O₁₉ were prepared with citrate sol–gel technique. The raw materials utilized in the present paper were barium carbonate, ferric citrate, cobalt nitrate and Ti(OC₄H₉)₄. The precursor were evaporated at 80 °C to produce a gel, and then heated at 120 °C for 24 h. The obtained powders was presintered at 450 °C for 5 h, and finally calcined at 600, 800, 1000, 1100, 1200 °C for 5 h, respectively, to obtain Ba(ZnTi)_xFe_{12–2x}O₁₉ ferrite crystalline powder.

* Corresponding author. Tel.: +86-371-7766196; fax: +86-371-7763822

E-mail address: zhanghaijun.tj@263.net (Z. Haijun).

The X-ray diffraction was carried out with a RAX-10 X-ray powder diffractometer to use Cu K α radiation. The electron micrographs were taken using a JSM-5610LV Scanning Electron Microscopy (SEM). A network analyzer (HP8753E) was employed to determine the values of ϵ' , ϵ'' , μ' , and μ'' at the frequency range of 0.2–6.0 GHz by using a reflection/transmission technique. For this, the ferrite–paraffin wax composites with 75% of ferrite by volume were prepared by homogeneously mixing the ferrite powder and toroidal-shaped samples of 3.0 mm inner diameter, 7.0 mm outer diameter and 2–4 mm length were prepared. The measured values of reflected and transmitted scattering parameters (S_{11} , S_{21}) were used to determine ϵ' , ϵ'' , μ' , and μ'' [13,14]. The intrinsic ferrite properties were isolated by the Lichtenecker effective medium expressions.

3. Results and discussion

The XRD patterns for the studied $\text{Ba}(\text{ZnTi})_x\text{-Fe}_{12-2x}\text{O}_{19}$ hexaferrite samples annealed at different temperature are shown in Fig. 1. At temperature over 800 °C, the product was identified to be M-type ferrite. At temperatures such as 450–600 °C, the products were identified to be mainly BaCO_3 and $\gamma\text{-Fe}_2\text{O}_3$. At temperature 150 °C, broad lines are observed, suggesting the presence of the amorphous state of $\text{Ba}(\text{ZnTi})_x\text{-Fe}_{12-2x}\text{O}_{19}$ precursor. The formation of $\text{Ba}(\text{ZnTi})_x\text{-Fe}_{12-2x}\text{O}_{19}$ by citrate sol–gel in our works starts at about 800 °C. Intermediate phases such as BaFe_2O_4 or any other phases of barium iron oxide are not observed, as is normally observed in samples synthesized by the ceramic route. This indicates that the solid-state reaction is exclusively heterogeneous, and hexaferrite phase formation proceeds by formation and growth at the expense of the existing phases, namely barium carbonate and maghemite. This is possible since, in the citrate sol–gel route of synthesis, mixing of cations takes place at

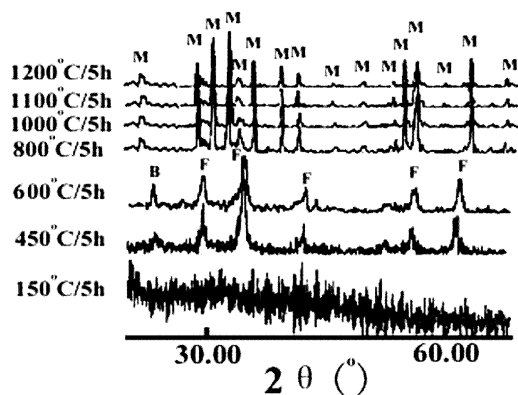
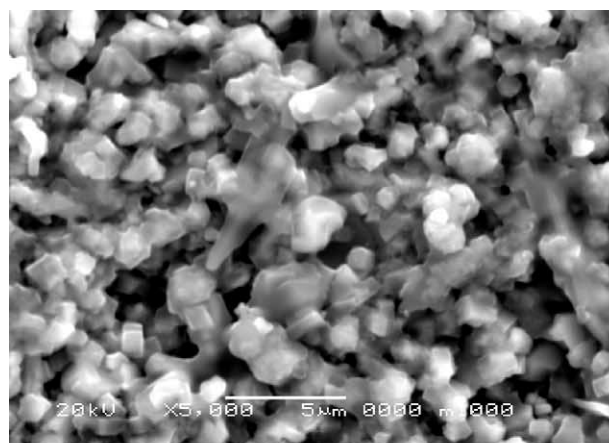
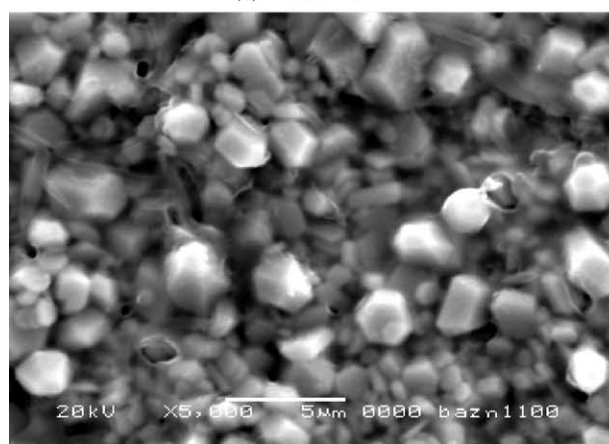


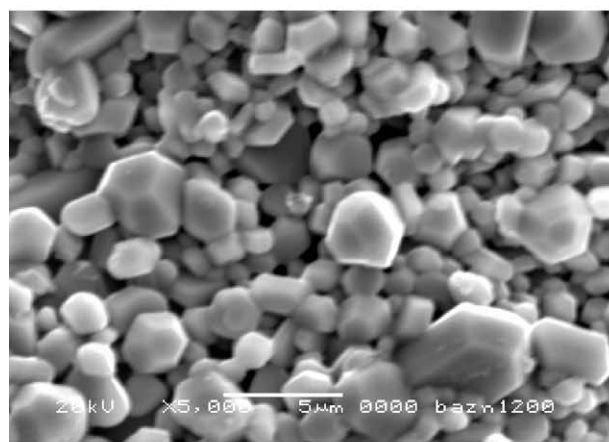
Fig. 1. X-ray diffraction pattern of the precursors heated at different temperature.



(a) 1000°C



(b) 1100°C



(c) 1200°C

Fig. 2. SEM photograph of the natural surface of $\text{Ba}(\text{ZnTi})_{1.0}\text{Fe}_{10.0}\text{O}_{19}$, sintered at 1000–1200 °C for 5 h.

the atomic level, thus reducing the paths of diffusion for various cations, as compared to the ceramic route where the diffusion distances are considerable. The small particle size of the precursor powder increases the diffusion area of the particles, thus enhancing the volume diffusion. As a matter of fact, the crystal

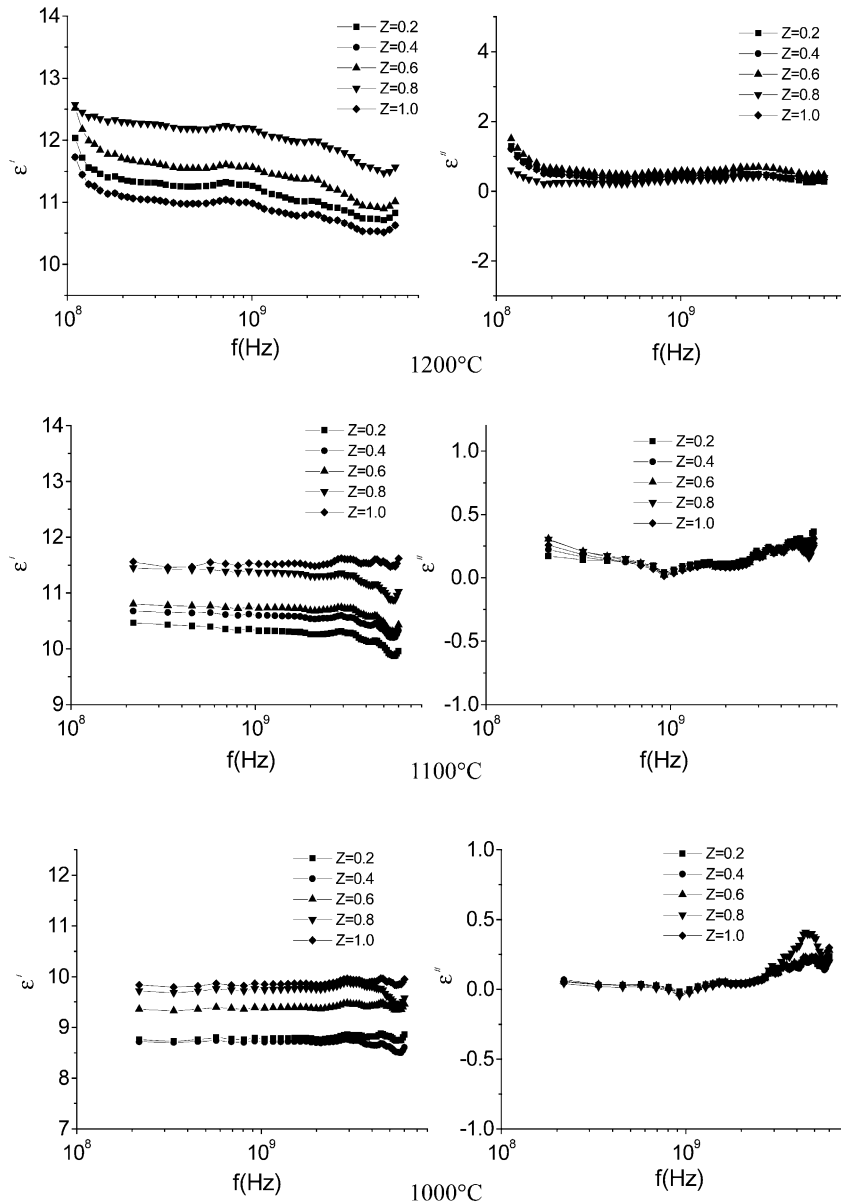


Fig. 3. Frequency dependence of ϵ' and ϵ'' of $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ annealed at 1000–1200 °C.

structure of Fe_2O_3 has an important role in the process of $\text{BaFe}_{12}\text{O}_{19}$ formation. $\text{BaFe}_{12}\text{O}_{19}$ has the magnetoplumbite structure, where the hexagonal unit cell consists of ten oxygen layers. The oxygen ions form a hexagonal or cubic close-packed lattice along the $[0\ 0\ 1]$ direction. $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) is a cubic spinel that has the chemical formula $\text{Fe}(\text{Fe}_{5/3}\square_{1/3})\text{O}_4$, where \square represents a cation vacancy. Its structure is similar to that of the S block (spinel structure with the chemical formula $\text{Fe}_6\text{O}_8^{2+}$) in $\text{BaFe}_{12}\text{O}_{19}$; therefore, $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) reacts with BaCO_3 easily to form single-phase $\text{BaFe}_{12}\text{O}_{19}$ at a lower temperature. However, if the intermediate is $\alpha\text{-Fe}_2\text{O}_3$, the reaction process needs a structure transformation, and a complete conversion of

the mixture to single-phase $\text{BaFe}_{12}\text{O}_{19}$ needs a higher annealing temperature [15].

Fig. 2 shows the microstructure of natural surface of $\text{Ba}(\text{ZnTi})_{1.0}\text{Fe}_{10.0}\text{O}_{19}$ ferrite calcined at 1000–1200 °C for 5 h in air. It indicates that the M-type ferrite particles are homogeneous hexagonal-shaped crystals, with an even size and a narrow distribution in crystal size. An increase in crystal grains size with annealing temperature is observed, the BaM grains size is about 1–2 μm in the case of 1000 °C, and about 2–3 μm , 3–4 μm for 1100 and 1200 °C, respectively.

The frequency dependence of ϵ' , ϵ'' for $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ ferrite is shown in Fig. 3. It can be seen from the figures that the values of the complex dielectric

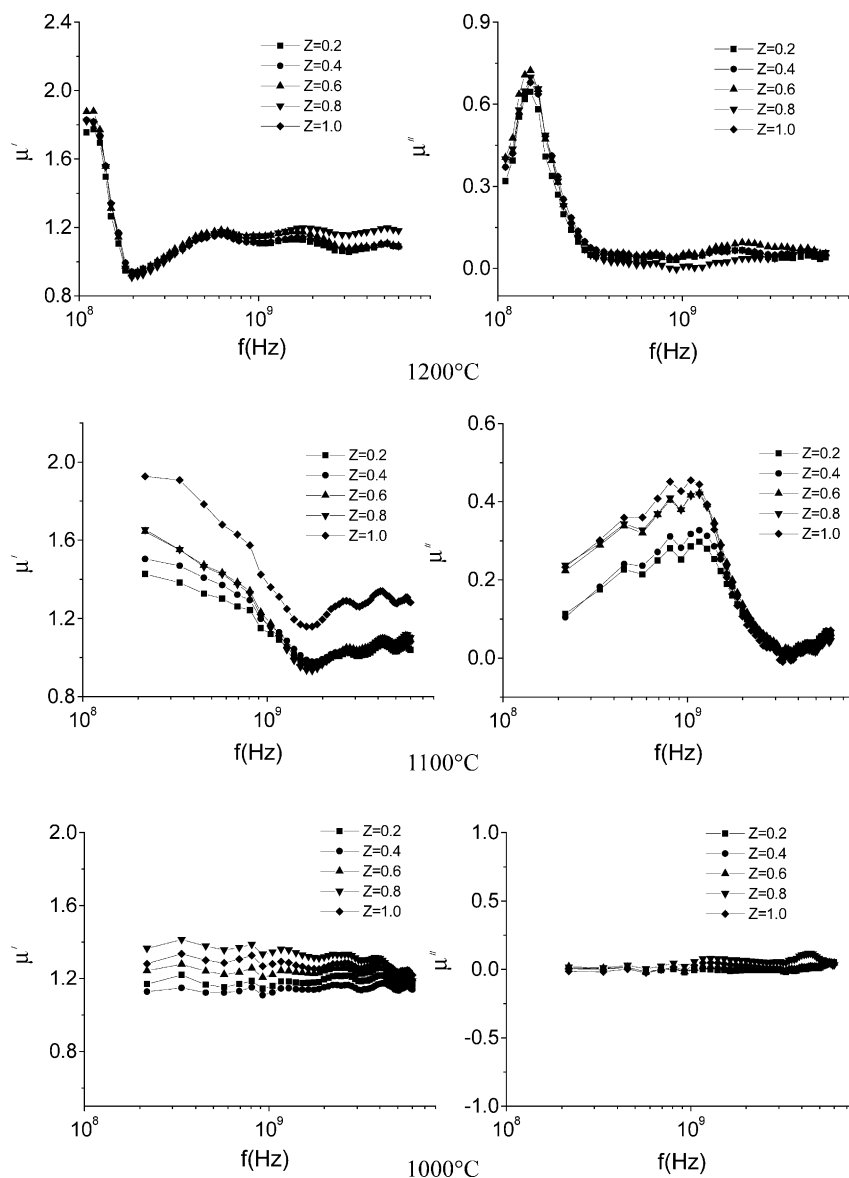


Fig. 4. Frequency dependence of μ' and μ'' of $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ annealed at 1000–1200 °C.

constant are found to decrease with increasing frequency for all $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ ferrites annealed at 1100–1200 °C. The decrease of the complex dielectric constant with an increase of frequency as observed in the case of $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ ferrites is a normal dielectric behavior of magnetoplumbite ferrites. This normal dielectric behavior was also observed by Ismel et al. [16] in the case of $\text{BaCo}_{2-x}\text{Zn}_x\text{Fe}_{16}\text{O}_{27}$, Praveen Singh et al. [17,18] in the case of CaCoTiM and CaNiTiM ferrites. However, for the samples annealed at 1000 °C, the real part of permittivity ϵ' shows insignificant variation in the whole measuring frequency, the imaginary part of permittivity ϵ'' exhibits a small peak at about 4–5 GHz. It also shows that the complex dielectric constant is composition as well as annealing temperature dependent, the higher the anneal-

ing temperature, the higher the dielectric constant, the maximum complex permittivity of $\text{Ba}(\text{ZnTi})_{0.8}\text{Fe}_{11.4}\text{O}_{19}$ ferrite annealed at 1200 °C is also observed. The dielectric properties of polycrystalline ferrite-wax composites arise mainly due to the interfacial polarization and intrinsic electric dipole polarization. The interfacial polarization results from the heterogeneous structure of ferrites comprising low-conductivity grains separated by higher-resistivity grain boundaries as proposed by Koops [19]. The polarization in ferrites has largely been attributed to the presence of Fe^{2+} ions which give rise to heterogeneous spinel structure. Since Fe^{2+} ions are easily polarisable, the larger the number of Fe^{2+} ions the higher would be the dielectric constant. The extent of Fe^{2+} ions in the ferrites largely depends upon the method of preparation. The high temperature

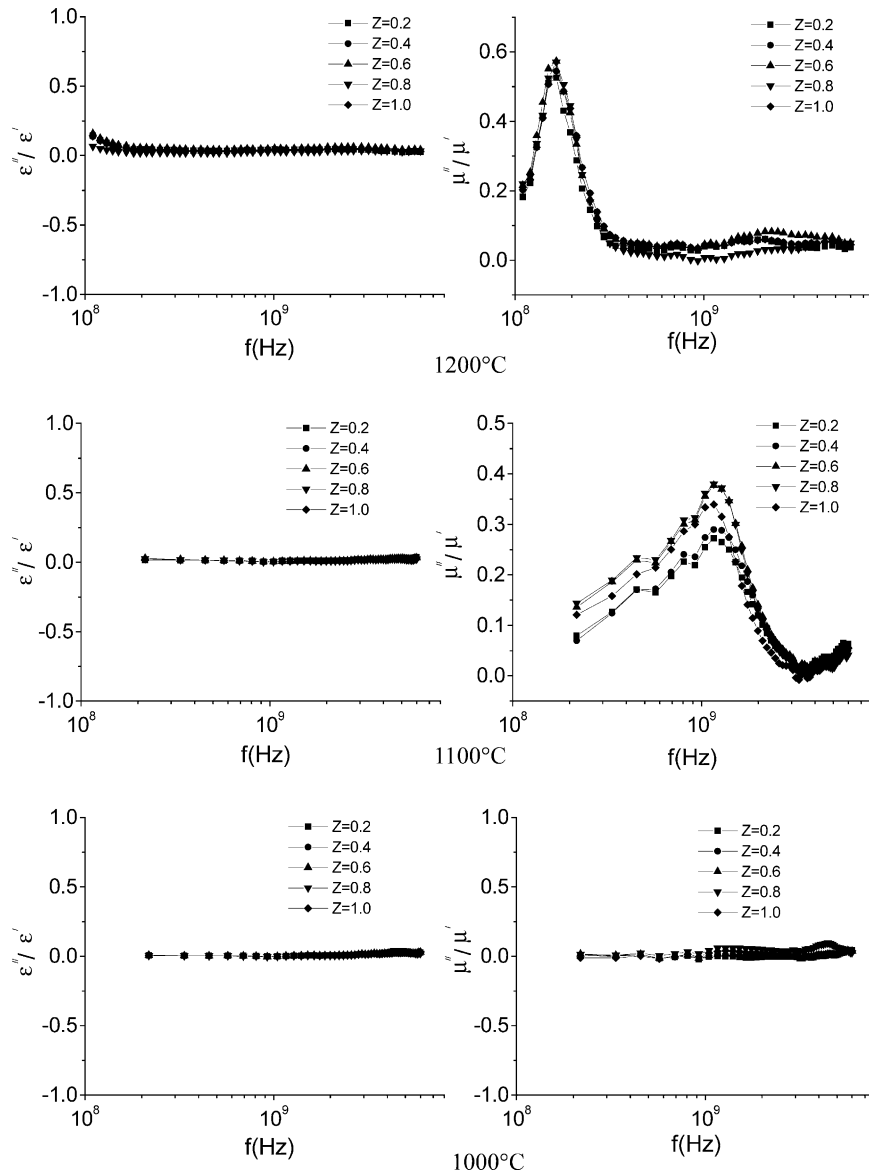


Fig. 5. Frequency dependence of dielectric and magnetic loss of $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$, annealed at 1000–1200 °C.

sintering proves deleterious as it results in Zn loss [20] from the ferrite due to volatilization and the consequent formation of Fe^{2+} ions. Thus, ferrites annealed at higher temperature are invariably likely to have more Fe^{2+} and, therefore, a higher dielectric constant. In addition to the sintering temperature, the amount of Zn in the samples also influences the dielectric properties of the ferrites in the following two ways: (a) ferrites with a larger zinc concentration are likely to contain relatively greater amount of Fe^{2+} as the probability of zinc evaporation would be more in these samples, and (b) zinc brings about perfection in the ferrite crystal structure [21]. These two effects play against each other in determining the sample properties. Thus, ferrite with x equals to 0.8 and 1.0 are likely to have higher values of ϵ' .

Fig. 4 illustrates the frequency dependence of the complex permeability for all samples annealed at 1000–1200 °C in the range from 0.1–6.0 GHz. μ' decreases with frequency increasing in the lower frequency until reaches a minimum value at about 200 MHz for samples annealed at 1200 °C and about 1.75 GHz for samples sintered at 1100 °C, and then it increases with frequency. However, μ' almost shows no variation with measuring frequency for the samples calcined at 1000 °C. Very obvious resonance phenomena are observed in μ'' spectrum for all samples annealed at 1100–1200 °C, and the resonance frequency is just annealing temperature dependent and shows no relation with composition, it shifts from 150 MHz to 1.16 GHz as the sintering temperature decreases from 1200 to 1100 °C for $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ ferrite. In fact, no

obvious resonance phenomena can be observed in μ'' spectrum for the samples annealed at 1000 °C. It is well known that the ferromagnetic resonance frequency of BaM ferrites can be given by the following relation:

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

Eq. (1) shows that the ferromagnetic resonance frequency is close related to the magnetocrystalline anisotropy field H_θ and H_ϕ of BaM ferrites, as a matter of fact that H_θ and H_ϕ is of close relation with the $\text{Zn}^{2+}\text{Ti}^{4+}$ substitution. It can be arrived a conclusion that the ferromagnetic resonance frequency must have relation with the $\text{Zn}^{2+}\text{Ti}^{4+}$ substitution. Thus the observed resonance phenomena in Fig. 4 can not attributed to ferromagnetic resonance and it is due to the domain-wall resonance. According to [22,23], the ferromagnetic resonance frequency of BaM ferrites manufactured by conventional ceramic methods and aqueous inorganic sol methods is about 43.5 and 45 GHz, respectively. The relation between complex permeability and domain-wall resonance frequency can be described as following:

$$(\mu_t - 1)^{1/2} f_r = \frac{\gamma M_s}{2\pi} \left(\frac{2\delta}{\pi \mu_o D} \right)^{1/2} \quad (2)$$

this expression shows that f_r is proportional to the saturation magnetization M_s . The observed enhancement of μ' with annealing temperature increasing in Fig. 4 can be ascribed to the increasing in the density of the samples which facilitates the movement of the spins as the number of pores which impede the wall motion are reduced. The increase in the sintering temperature also results in a decrease in the magnetic anisotropy by decreasing the internal stresses and crystal anisotropy which reduce the hindrance to the movement of the domain walls resulting thereby in the increased value of μ' .

Fig. 5 shows the frequency dependence of dielectric loss and magnetic loss in the range of 0.1–6 GHz for all samples annealed at 1000–1200 °C. The dielectric loss $\varepsilon''/\varepsilon''$, which represents the phase lag of the dipole oscillations with respect to the applied electric field, depends on the number and natural of ions present. The dielectric loss of $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ ferrite is very small with a value about zero and shows almost no significant variation with frequency in the whole measuring frequency. The magnetic loss μ''/μ' is annealing temperature as well as measuring frequency dependent, which shows a maximum value at about 165 MHz and 1.10 GHz for the samples annealed at 1200 and 1100 °C, with a value about 0.70 and 0.40, respectively.

For a microwave-absorbing layer backed by a metal plate, the normalized input impedance (Z_{in}) at the absorber surface is given by

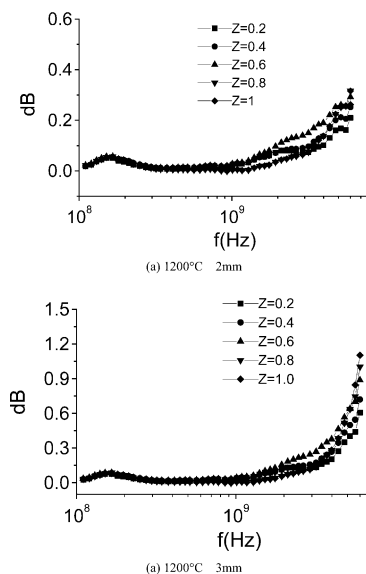


Fig. 6. The calculated reflection loss of $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ (1200 °C/5 h)-wax composite.

$$Z_{\text{in}} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left(j \frac{2\pi}{c} \sqrt{\mu_r \varepsilon_r} f d \right) \quad (3)$$

where μ_r is the complex permeability ($\mu_r' - j\mu_r''$), ε_r is the complex permittivity ($\varepsilon_r' - j\varepsilon_r''$), c is the velocity of electromagnetic waves in free space, f is the frequency, and d is the thickness of the absorber. The reflection coefficient (dB) is a function of the normalized input impedance (Z_{in}) which can be expressed as shown below,

$$R = 20 \lg |\Gamma| = 20 \lg \left| \frac{Z_{\text{in}} - 1}{Z_{\text{in}} + 1} \right| \quad (4)$$

The reflection coefficients can be calculated by using Eqs. (3) and (4). Fig. 6 shows the calculated reflection coefficients as a function of frequency, thickness for all $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ (1200 °C/5 h)-wax composite. It can be seen that reflection loss increases with frequency and thickness increasing, and which value is small in the whole measuring frequency. The result shows that it is improper to be microwave absorbing materials in 100 MHz–6.0 GHz for $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ ferrites.

4. Conclusion

$\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ hexaferrites are prepared by citrate sol–gel technique with precursors of ferric citrate, barium carbonate and metal nitrates. The results show that BaM ferrite can be prepared at about 800 °C. A minimum value at about 200 MHz, 1.75 GHz in μ' spectrum and very obvious resonance phenomena due to domain wall resonance in μ'' spectrum are observed for all samples annealed at 1200 and 1100 °C, respectively.

The calculation results of transmission line theory show that the reflection loss value is small for $\text{Ba}(\text{ZnTi})_x\text{-Fe}_{12-2x}\text{O}_{19}$ ferrites in 100 MHz–6.0 GHz.

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