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Introduction of Zn^{2+} in $BaCoTiFe_{10}O_{19}$ to tune electromagnetic parameters and improve microwave absorption properties

Wenjia Xing [a, b], Jing Chen [a, b], Hua Wang [a, b], Qingbo Fan [a, b], Qin Lei [a, b], Guangliang Xu [b, *]

[a] State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, PR China
[b] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China

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ABSTRACT

Zn^{2+} has been introduced to $BaCoTiFe_{10}O_{19}$ by sol-gel combustion method and the crystal system of $BaCoTiFe_{12}O_{19}$ can be well preserved in the process. Through study of magnetic parameters, we preliminarily expound the microwave-absorbing capacities, such as $BaZn_{0.2}Co_{0.8}TiFe_{10}O_{19}$ obtains preferable reflection loss (*RL*) with maximum saturation magnetization. Based on Debye dipolar relaxation of dielectric loss, the semicircles have been discussed in curves μ''-μ' about magnetic loss for the first time. The more semicircles curves μ''-μ' have, the better *RL* is. The $BaZn_{0.2}Co_{0.8}TiFe_{10}O_{19}$ achieves a satisfactory *RL* of −41.7 dB at 15.46 GHz with matching thickness of 2.1 mm. Its absorption bandwidth below −10 dB is 7 GHz (10.47–17.47 GHz) and the absorption bandwidth below −20 dB is 4.63 GHz (11.7–16.33 GHz). The matching thickness of $BaZn_{0.2}Co_{0.8}TiFe_{10}O_{19}$ is smaller approximately 1 mm than that of $BaCoTiFe_{10}O_{19}$. Therefore, investigation of the semicircle is significant to study magnetic loss and $BaZn_{0.2}Co_{0.8}TiFe_{10}O_{19}$ could be a promising microwave-absorbing material.

1. Introduction

With applying electronic system to microwave communication equipment, national defense, aerospace industry and so on, the gigahertz (GHz) band has rapidly developed. Therefore, the electromagnetic absorbing materials require more favorable properties [1–4]. Recently, broadening the absorption bandwidth, minimizing reflection loss (*RL*) [5], minishing weight [6] and miniaturizing particle size [7] have been studied extensively on absorbing materials. In practical application, the absorption bandwidth is one of characteristics that's most attractive for a microwave absorbing material. The static permeability μ'_0 closely relates to theoretical maximum frequency bandwidth, the equation as follows [8,9].

$$\begin{cases} \Delta\lambda \equiv \lambda_{max} - \lambda_{min} \le \dfrac{2\pi^2 \mu'_0 d}{|\ln(\rho_0)|} \\ \Delta f \propto \Delta\lambda \end{cases} \quad (1)$$

where ρ_0 is reflectivity, d is thickness, λ_{max} and λ_{min} are the wavelength upper and lower limits of bandwidth with ρ_0 respectively, Δf is frequency bandwidth. Equation (1) implies that the materials owning large μ'_0 can obtain a broad absorbing bandwidth with small d. In gigahertz (GHz) band, M-type barium ferrite ($BaFe_{12}O_{19}$, BaM) is considered to be one of the most promising microwave absorbing materials owing to the low cost, better stability, high natural resonant frequency (about 47.6 GHz) and excellent microwave magnetic loss [10–14]. The main microwave attenuation mechanism of BaM is magnetic loss. The magnetic loss includes domain wall movement and magnetization of spin relaxation [15,16]. In addition, resonance frequency is closely related to its magnetocrystalline anisotropy field, the relations as follows [9,16].

$$\begin{cases} f_r = \gamma H_a \\ \mu'_0 = \left(\dfrac{2M_s}{3H_a}\right) + 1 \end{cases} \quad (2)$$

For c-axis anisotropy, and

* Corresponding author.
E-mail address: xuguangliangswust@163.com (G. Xu).

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$$\begin{cases} f_r = \gamma\sqrt{H_\theta H_\varphi} \\ \mu'_0 = \left(\dfrac{M_s}{2H_\varphi}\right) + 1 \end{cases} \quad (3)$$

for c-plane anisotropy. Where γ is the gyromagnetic ratio, f_r is the resonance frequency, H_a is the anisotropy field of c-axis anisotropy, for c-plane anisotropy, H_θ and H_ϕ are out-of-plane anisotropy field and in-plane anisotropy field respectively, μ'_0 is the static permeability. Based on formula (2), the tremendous value H_a of BaM leads to very high resonance frequency. Taking the place of Fe^{3+} with other metal ions is a good way to adjust its anisotropy field [11,17,18], which is conducive to applying to different microwave absorption band. For BaM, L. Du et al. [19] have verified that the resonance frequency can be shifted to the X band (8–12.4 GHz) through replacing Fe^{3+} with Co^{2+} and Ti^{4+}. In addition, Sözeri et al. [20] have confirmed that the resonance frequency can be moved to the Ku band (12.4–18 GHz) when replacing some Fe^{3+} ions with Zn^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+} and Ti^{4+}. The magnetocrystalline anisotropy of $BaCo_xTi_xFe_{12-2x}O_{19}$ can be tuned from axial to planar with increasing x [17,21] and it means that the f_r can be tuned to lower frequency.

Keeping the virtues of $BaCoTiFe_{10}O_{19}$, broadening its absorbing band and tuning its resonance frequency are the focus of the study. $BaCoTiFe_{12}O_{19}$ and $BaZnTiFe_{12}O_{19}$ possess similar saturation magnetization and coercivity, what's more, the *RL* curves of $BaCoTiFe_{12}O_{19}$ and $BaZnTiFe_{12}O_{19}$ have same variation trend [20]. Nonmagnetic Zn^{2+} and Ti^{4+} can occupy some special sites to affect the saturation magnetization [9,21–24]. Kong et al. [9] have confirmed that the anisotropy field, H_a or H_ϕ, would be weakened by putting Zn^{2+} ions in sites located Fe^{3+} ions. Therefore, $BaZn_xCo_{1-x}TiFe_{10}O_{19}$ (BZCTM) could obtain relatively large saturation magnetization (M_s) with the anisotropy field slightly changing. Based on Equation (2) or Equation (3), enlarging the M_s is beneficial to increase of μ'_0, which can acquire a broad absorption bandwidth. In this paper, the electromagnetic parameters and microwave absorbing properties of BZCTM are systemically studied with the frequencies ranging from 0.5 to 18 GHz.

In addition, for dielectric loss materials, Debye dipolar relaxation helps to enhance microwave absorption properties [25–27] and some studies [28,29] have proved Cole–Cole semicircles in the plot of ε''-ε'. Compared with dielectric loss, the magnetic loss maybe also has a similar conclusion. We will study the semicircles in magnetic loss materials to establish some connections between semicircle and *RL*.

2. Experimental

2.1. Preparation of samples

The powders of BZCTM (x = 0, 0.1, 0.2, 0.4, 0.6 and 0.8) were fabricated by the sol–gel combustion technique. The stoichiometric $Fe(NO_3)_3\cdot 9H_2O$ (AR), $Ba(NO_3)_2$ (AR), $Ti(OC_4H_9)_4$ (AR), $Co(NO_3)_2\cdot 6H_2O$ (AR) and $Zn(NO_3)_2\cdot 6H_2O$ (AR) were dissolved in 50 mL deionized water with magnetic stirring to synthesize 0.005 mol samples. After solutes completely dissolved, the 0.065 mol citric acid (AR) was added into the solution and entirely dissolved. In order to adjust the pH value to 7, ammonia solution (AR) was added by dropwise with stirring. Subsequently, the adjusted solution was heated up to 100 °C with stirring to obtain dried gel. Keep on heating, the dried gel would burn up in a self-propagating combustion manner and some powders could be gained. These powders were heated up to 650 °C with the heating rate 5 °C/min and pre-calcined 4 h, and then heated up to 1100 °C with the speed 3 °C/min and calcined 4 h to obtain the BZCTM powders.

2.2. Preparation of vector network analyzer's samples

Due to the paraffin wax (PW) almost no contribution to microwave absorption [33], BZCTM was mixed with PW to investigate microwave absorption properties. The composites were prepared by mixing BZCTM powders with PW according to the mass ratio of 85:15. Subsequently, the mixture was dissolved in xylene and ultrasound for 30min. Finally, the solution was kept in the oven at 56 °C to remove the solvent completely. Under the 3.0 pa for 5 min, the mixture was pressed into a toroidal shape with inner diameter of 3.00 mm, outer diameter of 7.00 mm and thickness is approximately 2.0 mm.

2.3. Characterization of samples

The phase composition of samples was studied by X-ray diffractometer (XRD, X'Pert PRO, PANalytical, the Netherland) with Cu Kα source (λ = 1.5406 Å). The size-distribution and morphology were characterized by the field emission scanning electron microscopy (FE-SEM, Zeiss Ultra 55, Germany). The magnetic hysteresis (M–H) loops of BZCTM powders were measured by the vibrating sample magnetometer (VSM, BKT-4500Z, China) with the maximum magnetic field of 6 kOe. The relative permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) were measured by a vector network analyzer (Agilent Technologies, E8363A, USA) adopted the coaxial measurements in the range of 0.5–18 GHz.

3. Results and discussion

The XRD patterns of BZCTM powders are shown in Fig. 1. All diffraction peaks are well consistent with the BaM (JCPDS Card No. 039-1433) and no other phase is detected. It means that introducing Zn^{2+} into $BaCoTiFe_{10}O_{19}$ not destroys its original phase [17]. As shown in Table 1, the lattice constants of BZCTM have a little fluctuation, which may be due to the radius value of Zn^{2+} (r^{2+}_{Zn} = 0.74 Å) [22] very closes to that of Co^{2+} (r^{2+}_{Co} = 0.745 Å) [31–33]. what's more, the Co^{2+} [31,34,35] and Zn^{2+} [22,36] have different occupying sites.

For x = 0, 0.1, 0.2, 0.4 and 0.8, the size and morphology of BZCTM powders have been studied by FESEM. It can be seen from Fig. 2

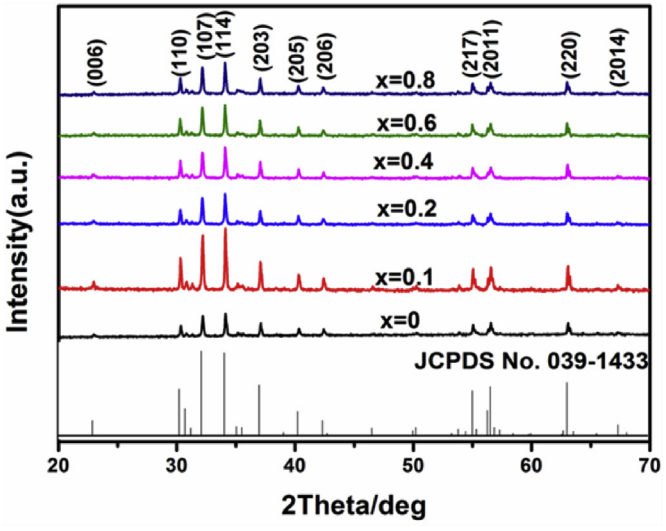

Fig. 1. XRD patterns of $BaZn_xCo_{1-x}TiFe_{10}O_{19}$ composites.