Journal of Magnetism and Magnetic Materials 385 (2015) 407–411

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Wideband and enhanced microwave absorption performance of doped barium ferrite

Pingyuan Meng [a], Kun Xiong [a], Kui Ju [b], Shengnan Li [a], Guangliang Xu [a,*]

[a] State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China
[b] Guizhou Institute of Metallurgy and Chemical Engineering, Guiyang 550002, PR China

ARTICLE INFO

Article history:
Received 9 October 2014
Received in revised form
26 December 2014
Accepted 27 February 2015
Available online 28 February 2015

Keywords:
Barium ferrite
Sol–gel combustion
Wideband
Reflection loss

ABSTRACT

To achieve stronger microwave attenuation and larger bandwidth in electromagnetic absorber, the nickel ions (Ni^{2+}) and manganese ions (Mn^{2+}) were employed to partially replace the cobalt ions (Co^{2+}) in $BaCoTiFe_{10}O_{19}$, and the doped barium hexaferrite ($Ba(MnNi)_{0.2}Co_{0.6}TiFe_{10}O_{19}$ and $Ba(MnNi)_{0.25}Co_{0.5}TiFe_{10}O_{19}$) powders were synthesized via the sol–gel combustion method. Subsequently, the microwave absorbing composites were prepared by mixing the ferrite powders with the paraffin. The X-ray diffraction (XRD) patterns of the doped ferrites confirmed the formation of the M-type barium ferrite, and no other types of barium ferrite could be found. Based on the electromagnetic parameters measured by the vector net-analyzer, it was found that the composite ($Ba(MnNi)_{0.2}Co_{0.6}TiFe_{10}O_{19}$) possessed a minimum reflection loss of −52.8 dB at 13.4 GHz with a matching thickness of 1.8 mm and the bandwidth below −15 dB was 5.8 GHz. Moreover, the maximum attenuation of $Ba(MnNi)_{0.25}Co_{0.5}TiFe_{10}O_{19}$ could reach −69 dB when its thickness was 1.8 mm, and also the bandwidth less than −20 dB was ranging from 13.2 GHz to 18 GHz. Thus, $Ba(MnNi)_{0.2}Co_{0.6}TiFe_{10}O_{19}$ and $Ba(MnNi)_{0.25}Co_{0.5}TiFe_{10}O_{19}$ could be the good microwave absorbers, which have great potentials to be applied in the high frequency fields of the microwave absorbing materials.

1. Introduction

Concern about the electromagnetic interference and electronic countermeasures have become crucial issues in military fields, and as a result, much more researches in recent years have focused on electromagnetic-absorber technology [1–6]. The electromagnetic wave absorbers can effectively reduce the reflection of electromagnetic signals, which could improve the battlefield survivability of military aircrafts and vehicles, as electromagnetic wave absorbing materials coating on the surfaces of military equipments. However, the absorbers for a single frequency cannot meet the demands of the updated technology, while the materials which possess broad bandwidth, minimum reflection loss (RL) and lightweight mass (or small thickness) have been extensively studied recently [7].

M-type barium hexagonal ferrite ($BaFe_{12}O_{19}$, BaM) is considered as one of the promising candidate materials for up-to-date microwave absorption in the GHz range, which is due to its low cost, good stability, high natural resonance frequency (about 47.6 GHz) and excellent microwave magnetic loss [8–11]. As is well known, it is an effective way to change the microwave absorption performance of BaM by using other metal ions to replace the ferric ions (Fe^{3+}) [12–17]. Tehrani and his co-workers [4] have studied the substituted M-type barium hexagonal ferrite $BaMg_{0.25}Mn_{0.25}Co_{0.5}Ti_{1.0}Fe_{10}O_{19}$, and the bandwidth of 4.5 GHz below −20 dB at a thickness of 2.7 mm was obtained. Sun and his partners [3] have researched Ce-substituted barium ferrite $BaCe_{0.05}Fe_{11.95}O_{19}$, and the results showed a minimum reflection loss value of −37.4 dB with a matching thickness of 3.5 mm. Dong et al. [8] have reported that the $BaCo_{0.3}Ti_{0.3}Fe_{11.4}O_{19}$ exhibits a minimal RL (−47 dB) at a thickness of 0.8 mm. Thus, choosing appropriate ions to substitute BaM is significance to improve the absorption performance of the ferrite.

In the previous work, it had been demonstrated that the Mn^{2+} and Ni^{2+} could enhance the absorption properties of $BaCoTiFe_{10}O19$ composites [18,19]. Especially, it could also broaden the absorbing bandwidth as the Ni^{2+} substituted [7]. Thus, the microwave absorption performances of $Ba(MnNi)_{0.2}Co_{0.6}TiFe_{10}O_{19}$ (MNCF1) and $Ba(MnNi)_{0.25}Co_{0.5}TiFe_{10}O_{19}$ (MNCF2) were preliminary researched in present work, as Mn^{2+} along with Ni^{2+} was employed to partially occupy the place of cobalt ions (Co^{2+}) in $BaCoTiFe_{10}O_{19}$. The phase composition and crystalline structure of

* Corresponding author.
E-mail address: xuguangliang@swust.edu.cn (G. Xu).

http://dx.doi.org/10.1016/j.jmmm.2015.02.059
0304-8853/

MNCF1 and MNCF2 were evaluated. Moreover, the magnetic properties and the microwave absorption properties of doped ferrites were detailedly investigated in the frequency range of 0.5–18 GHz.

2. Experimental

2.1. Preparation of doped ferrites powders

The powders of $Ba(MnNi)_{0.2}Co_{0.6}TiFe_{10}O_{19}$ and $Ba(MnNi)_{0.25}Co_{0.5}TiFe_{10}O_{19}$ were synthesized via the sol–gel combustion method. All of the raw materials in this experiment are analysis reagents and made in Aladdin Industrial Corporation of China. As starting materials, appropriate amount of $Fe(NO_3)_3\cdot 9H_2O$, $Ba(NO_3)_2$, $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Ti(OC_4H_9)_4$ and $Mn(NO_3)_2$ were dissolved in 100 mL deionized water by stirring it constantly using a magnetic stirrer. After they were dissolved completely, 100 mL citric acid solution (0.65 M) was added into the solution, and then ammonia solution was added dropwise with vigorous stirring to maintain the pH value of the solution at 7. Subsequently, the neutralized solution was heated at 100 °C with continuous magnetic stirring to obtain the dried gel. With further heating, the dried gel would burn up in a self-propagating combustion manner, and some brown powders could be obtained. Finally, these brown powders were pre-heated at 450 °C for 4 h, and then calcined at 1100 °C for 4 h to obtain the $Ba(MnNi)_{0.2}Co_{0.6}TiFe_{10}O_{19}$ (MNCF1) and $Ba(MnNi)_{0.25}Co_{0.5}TiFe_{10}O_{19}$ (MNCF2).

2.2. Preparation of doped ferrites composites

The ferrites composites were prepared by mixing doped ferrites powders with the paraffin according to a mass ratio of 85:15. Subsequently, the mixture was dissolved in xylene and ultrasonicated for 30 min. Finally, the mixture was kept in the oven at 70 °C to remove the solvent completely and the dried mixture was hot pressed at 220 °C under 5.5 MPa for 30 min into a circular cylinder with an inner diameter of 3.0 mm, outer diameter of 7.0 mm and thickness ranged from 1.5 mm to 2.0 mm.

2.3. Measurement of properties

The phase composition of doped ferrites powders was identified by the X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V., The Netherlands) equipment, with Cu Kα radiation ($\lambda=1.540598$ Å, 35 kV and 25 mA) in the range of 20–70° and a scan rate of 6°/min. The size and morphology of doped ferrites powders were observed by using the field emission scanning electron microscopy (FE-SEM, Zeiss Ultra 55, Germany). The vibrating sample magnetometer (VSM) was used to measure magnetic hysteresis (M–H) loops of the ferrites powders. Finally, the complex permittivity and permeability of MNCF1 and MNCF2 composites in the frequency range of 0.5–18 GHz were determined by a network analyzer (Agilent Technologies, E8363A) using the coaxial measurements, and the reflection loss of the samples was calculated from the relative complex permeability and permittivity with a given frequency range and a given absorber thickness (d) by the following equation [20]:

$$RL = 20\log\left|(Z_{in}-1)/(Z_{in}+1)\right| \quad (1)$$

Z_{in} is determined as:

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

where Z_{in} is the input impedance of absorber, ε_r and μ_r are complex permittivity and permeability of the composite, respectively, f is the microwave frequency and c is the velocity of light in free space. From the reflection loss, the microwave performance of the composites was investigated.

3. Results and discussion

3.1. Microstructure and magnetic characteristics

The XRD patterns of MNCF1 and MNCF2 powders are presented in Fig. 1. All the diffraction peaks are very consistent with those of BaM, and no second phase can be detected, indicating that the substitution of Mn–Ni seems to arrange in the hexagonal structure and also will not affect its original phase.

The size and morphology of the synthesized MNCF1 and MNCF2 powders were further examined by the FE-SEM. Overall view of the SEM imagines in Fig. 2, the ferrite particles appeared fine grain growth with some agglomeration and many small ferrites grains had a size ranging in 100–400 nm. The majority of the doped ferrites grains displayed an irregular shape except some bigger crystals, which have a significant hexagonal-shape.

The hysteresis loops of doped BaM ferrites are presented in Fig. 3. It has been reported that the coercive force (H_c) of pure BaM ferrite can reach 4500 Oe due to its strong uniaxial magnetocrystalline anisotropy along c-axis [4]. Fig. 3 demonstrates the H_c decreases to about 1000 Oe with the substitution of Mn, Ni, Co and Ti, and also slightly increases when the amount of $Mn^{2+}Ni^{2+}$ varied from 0.2 to 0.25, which may be attributed to the enhancement of uniaxial anisotropy along c-axis resulting from the different replacing sites of Fe^{3+} [12].

3.2. Microwave absorption characteristics

Generally, the real parts of complex permittivity and permeability symbolize the storage capability of electric and magnetic energy, and the imaginary parts represent the loss of electric and magnetic energy [12,21]. To reveal the microwave absorbing property, the complex relative permittivity ($\varepsilon=\varepsilon'+j\varepsilon''$) and the complex relative permeability ($\mu=\mu'+j\mu''$) for the ferrites–paraffin composites are investigated in Figs. 4 and 5. As shown in Fig. 4a, the real parts of complex permittivity (ε') for both

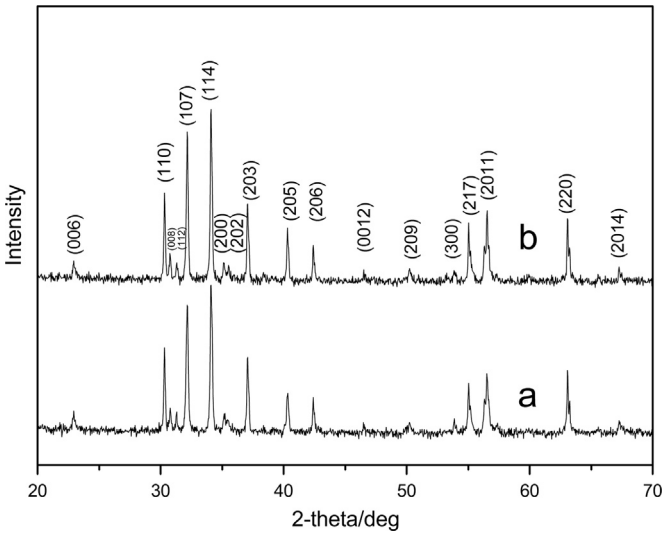

Fig. 1. X-ray diffraction patterns for the powders: (a) $Ba(MnNi)_{0.2}Co_{0.6}TiFe_{10}O_{19}$ and (b) $Ba(MnNi)_{0.25}Co_{0.5}TiFe_{10}O_{19}$.