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Preparation and microwave absorption of M type ferrite nanoparticle composites

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The sol-gel method was used to obtain M type $BaFe_{12}O_{19}$ ferrite nanoparticles. Rod like and flake like ferrite nanoparticles can be successfully fabricated by controlling the heating process of the precursor. The phase attributes, morphology and grain size of $BaFe_{12}O_{19}$ ferrite were characterized by TEM and XRD. The complex permittivity and permeability of ferrite epoxy resin composites were measured in the Ku waveband (12.4–18 GHz). Ferrite composites containing short carbon fibres have also been fabricated in order to obtain higher complex permittivities of the composites. The reflectivities of these ferrite composites were calculated according to the measured electromagnetic parameters. The results show that the microwave absorption properties of ferrite composites can be effectively improved by filling them with short carbon fibres.

Keywords: *ferrite nanoparticles; sol-gel method; carbon fibres; microwave absorption*

1. Introduction

Electromagnetic wave absorbing materials in the GHz range have attracted much attention in recent years with the development of GHz microwave communication, radar detection and other industrial applications. These absorbing materials can be manufactured by a number of magnetic and dielectric materials in powder forms, loaded in various kinds of polymeric binders. Various electromagnetic wave absorbing materials can be designed by using the dispersion characteristic of the complex permittivity and permeability [1–5]. Ferrite is one of materials used as an electromagnetic

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wave absorber, and a number of studies have been reported on the dependence of the electromagnetic wave absorption properties on their composition [6–12]. However, a pure ferrite microwave absorber is insufficient to achieve wideband absorption. In this work, emphasis has been laid on the synthesis of nanocrystalline $BaFe_{12}O_{19}$ ferrite powders and improving the dielectric properties of ferrite composites.

In the present study, M type ferrite nanoparticles were obtained by adopting the citrate sol-gel method. Various heating processes of the precursors were used to obtain different morphologies of nanoparticles. The flake-like nanoferrite was selected to produce ferrite epoxy resin composites. In order to improve the dielectric properties of ferrite composites, short carbon fibres (T700) were filled into the composites. The electromagnetic parameters of the ferrite composites were measured in the Ku wave-band by a network analyzer, and the microwave reflectivity of a single layer coating of the ferrite composites was calculated.

2. Experimental

M type $BaFe_{12}O_{19}$ hexaferrites were fabricated by the citrate sol-gel technique. The starting materials were $Ba(NO_3)_2$, $Fe(NO_3)_3{\cdot}9H_2O$ and citric acid. In a typical procedure for the preparation of $BaFe_{12}O_{19}$, firstly, aqueous solutions of barium and ferric salts were obtained separately by dissolving the salts in distilled water, and then added together in stoichiometric proportions. Solution of citric acid was added to the aqueous salt solution in an appropriate proportion under constant stirring and pH of the solution was adjusted to 7.0 with ammonia. The solution was then heated to 80 °C and maintained at that temperature for 3 h in a water bath. Finally, the solution was dried at 100 °C to form a dry gel. To obtain different structural features of ferrites, the dried gel precursor was treated by various heating methods in a muffle furnace. The precursor was heated to 900 °C at the rate of 50 °C/h, and then calcined at the same temperature for 4 h (sample A). Other samples were fabricated by a double heat-treatment method. First, the precursor was pre-heated at 450 °C for 3 h, and then the it was heated to 900 °C at the rate of 50 °C/h and calcined at 900 °C for 4 h to form ferrite sample B. Ferrite sample C was obtained by a similar method as sample B; the only difference was that the pre-heated product was rapidly heated to 900 °C.

The X-ray diffraction patterns of the ferrite powder were obtained with an X-ray powder diffractometer with CuK_α radiation (D/max-2550). The morphology of the crystal grain was observed under a transmission electron microscope (H-800). The electromagnetic parameters, complex permittivity and permeability, were measured by a network analyzer (Agilent E8363B) in the Ku waveband. In order to measure the electromagnetic parameters of composites, rectangular samples were made from the ferrite sample C and epoxy resin composite with 60 wt. % of ferrite. To obtain material of higher permittivity, ferrite composite samples containing 0.2 wt. % of short carbon fibres (3 mm long) were also obtained.

3. Results and discussion

3.1. Characterization of samples

XRD patterns of the ferrites samples synthesized by the sol-gel route are shown in Fig. 1. They show that the heating method affects the structural features of ferrite products. M type hexaferrite $BaFe_{12}O_{19}$ and α-Fe_2O_3 phases can be detected in sample A which fabricated by direct heating of dried precursors to 900 °C. Curves b and c in Fig. 1 show that pure crystalline M type ferrite can be obtained when the precursors are first preheated at 450 °C for 3 h, and then calcined at 900 °C.

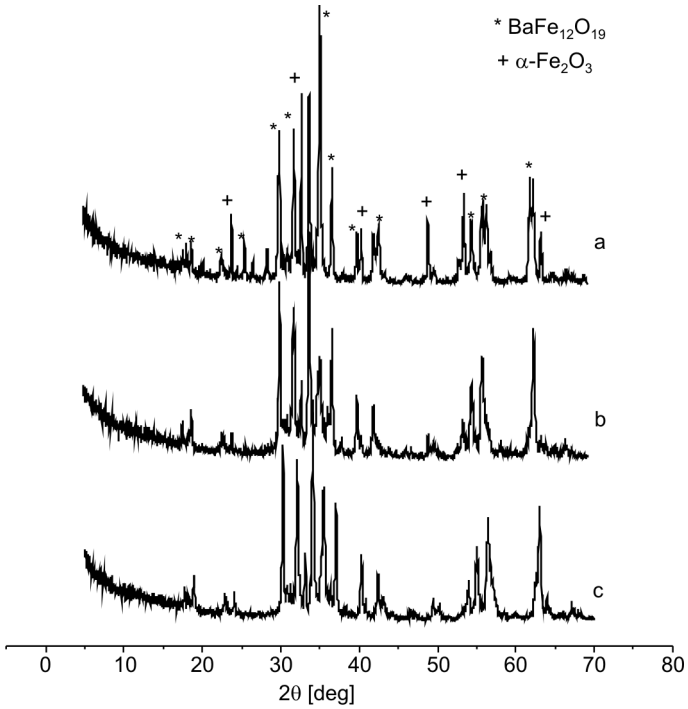

Fig. 1. XRD patterns of the ferrite samples: a) sample A, b) sample B, c) sample C

When the dried precursors are heated, the following reactions occur [8]:

$$\text{Dried precursors} \rightarrow \gamma\text{-}Fe_2O_3 + Ba^{2+}$$

$$\gamma\text{-}Fe_2O_3 + Ba^{2+} \rightarrow BaFe_2O_4$$

$$BaFe_2O_4 + 5\gamma\text{-}Fe_2O_3 \rightarrow BaFe_{12}O_{19}$$

First of all, precursors decompose and produce γ-Fe_2O_3, and then the reaction proceeds as shown in the above equations during the subsequent heat treatment. Finally,

the ferrite $BaFe_{12}O_{19}$ is obtained. However, when precursors are heated to 900 °C directly, α-Fe_2O_3 forms a stable phase and does not react with Ba^{2+} at 900 °C. As a result, a small amount of residual exists in sample A. However, the pre-heat treatment at 450 °C can effectively prevent precursors from producing α-Fe_2O_3 [13, 14].

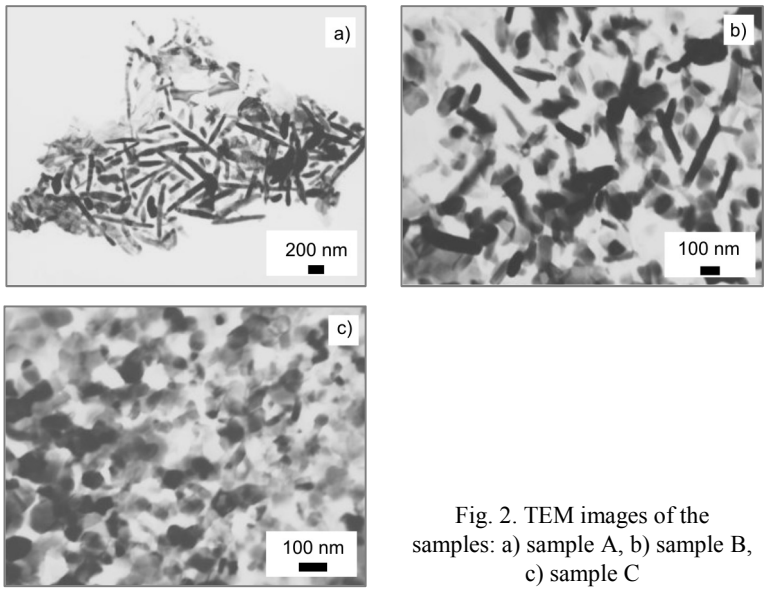

Fig. 2. TEM images of the samples: a) sample A, b) sample B, c) sample C

The morphology of the ferrite particles was examined by TEM. Homogeneous rod-like particles 60 nm in diameter, 0.7–1.0 μm long were found in sample A, as shown in Fig. 2a. Figure 2b shows that the particles of sample B are both rod-like and flake-like. However, the rod-like particles are not as homogeneous as sample A. The particles of sample C are mostly flake-like, and the average size of the grains is about 80 nm. The crystal morphology is determined by the growth rate of every crystal face, according to the crystal growth mechanism described in [15, 16]. Under slow heating, the crystallization time is enough long and the growth rate is higher along the long-axis for the hexaferrite. Thus a slow heating rate is conducive to fabrication of one-dimensional nanorods [17, 18] but a detailed mechanism of formation of the as-prepared rods and flakes is still under investigation.

3.2. Microwave absorption

The dependences of the complex permittivity and permeability of ferrite composites on frequency are shown in Figs. 3 and 4. Figure 3 represents the frequency dependences of the real part ε' and the imaginary part ε'' of the complex permittivity of the ferrite composite (M) and the ferrite composite filled with short carbon fibre (MC), respectively. The values of ε' and ε'' for the composite MC are higher than for the

composite M in the Ku waveband. The dielectric properties of polycrystalline ferrite composites arise mainly from the interfacial polarization and the intrinsic electric dipole polarization. However, the dielectric properties of the composite MC arise not only from the polarization of ferrite but also from the electric dipole polarization of short carbon fibres [19].

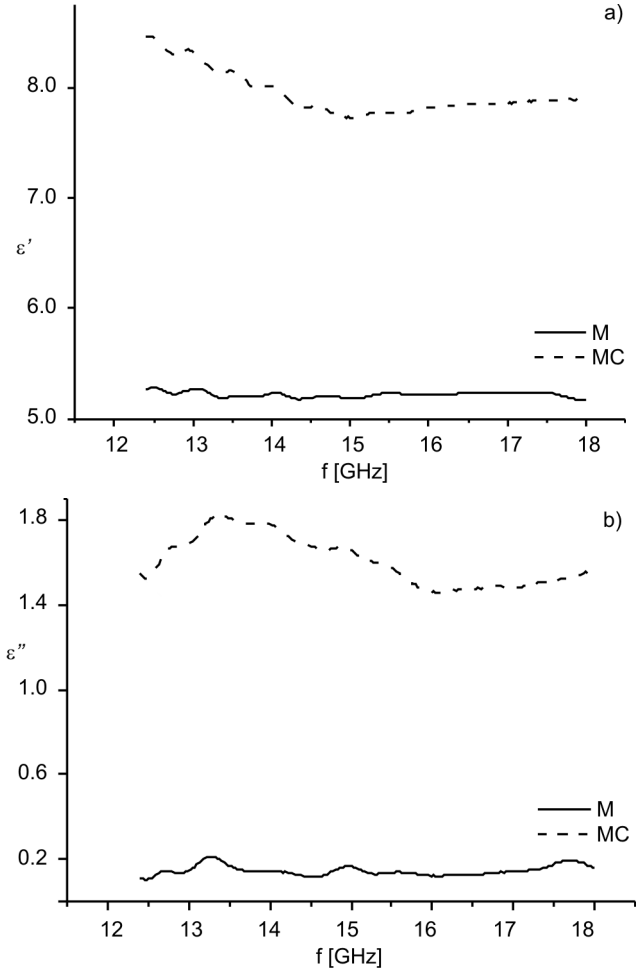

Fig. 3. Dependences of complex permittivity of ferrite composites on frequency: a) real part, b) imaginary part

It is seen from Fig. 4 that the values of μ' and μ'' of the complex permeability of the ferrite composite M and the composite MC are similar over the considered frequency range. The reason is that addition of carbon fibre has affects the magnetic properties of the composites.

The reflectivity of the incident electromagnetic wave normal to the planar single-layer coated on a metal plate is given as

$$R = 20\lg\left|\frac{\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left(j\frac{2\pi f}{c}\sqrt{\mu_r\varepsilon_r}d\right)-1}{\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left(j\frac{2\pi f}{c}\sqrt{\mu_r\varepsilon_r}d\right)+1}\right| \tag{1}$$

Here d, ε_r and μ_r are the thickness of the coating, the relative complex permittivity and the permeability of the composite, respectively [15].

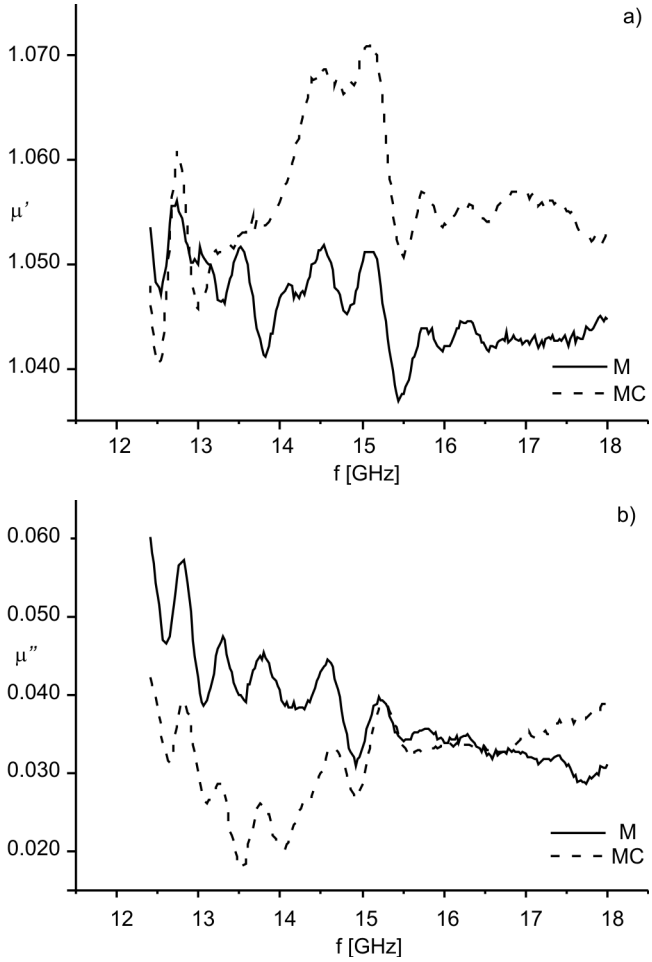

Fig. 4. Dependences of complex permeability of ferrite composites on frequency: a) real part, b) imaginary part

Figure 5 shows the predicted microwave absorption properties of a single layer coating 2 mm thick for the composite M and composite MC, according to Eqs. (1). It is observed that the reflective loss of the ferrite composite M is worse than that of MC.

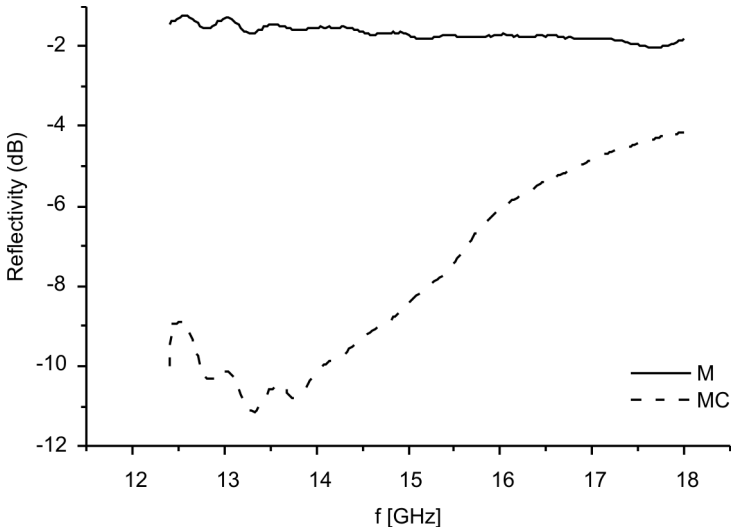

Fig. 5. Absorption curves of ferrite composite coatings

However, the absorption properties of the composite MC, which is filled with short carbon fibres, are improved obviously. Its reflectivity decreases as frequency increases, for frequencies below 13.3 GHz, and begins to increase gradually for frequencies above 13.3 GHz. The reflectivity is about –11.0 dB at 13.3 GHz, and –4.2 dB at 18 GHz. The absorption bandwidth lower than –10.0 dB is 1.4 GHz, which is from 12.7 GHz to 14.1 GHz. The reason that the absorption properties of the composite MC are better than those of the composite M is that short conductive carbon fibres in ferrite composite can act as electric dipoles and resonate with the incident wave. Adding short carbon fibres can increase the dielectric loss of the considered composites.

4. Conclusion

M type $BaFe_{12}O_{19}$ hexaferrite nanoparticles were successfully synthesized by the citrate sol-gel process. Rod like and flake like nanoparticles were obtained by various heating methods. Ferrite composites containing short carbon fibres were designed to test the electromagnetic parameters of the composites. The results show that addition of short carbon fibres can effectively improve the microwave absorption properties of M type ferrite nanocomposites. Absorption bandwidth lower than –10.0 dB of the composite is 1.4 GHz, between 12.7 GHz and 14.1 GHz. The method of preparation and design may potentially be applied to produce light weight and high performance absorption materials.

Acknowledgements

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