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Microwave absorbing properties of the ferrite composites based on graphene

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ABSTRACT

The graphene/(1−x)$BaFe_{12}O_{19}$/$CaFe_2O_4$/x$CoFe_2O_4$ ferrite composite powders were successfully synthesized by a deoxidation technique. The phase composition, morphology and electromagnetic properties of the composites were characterized by various instruments. The experimental results show that the graphene/(1−x)$BaFe_{12}O_{19}$/$CaFe_2O_4$/x$CoFe_2O_4$ ferrite composites exhibit evidently enhanced microwave absorbing performance in comparison with the graphene/(1−x)$BaFe_{12}O_{19}$/$CaFe_2O_4$ and graphene/$CoFe_2O_4$ composites and the minimum reflection loss is −36.8 dB at 9.9 GHz with a thickness of 2.9 mm.

1. Introduction

In recent years, with the requirement of solving the enlarged electromagnetic interference (EMI) problems, much attention has been concentrated on the effective electromagnetic (EM) wave absorption materials with the performances of wide frequency range, strong absorption, low density, low cost, and high resistivity [1]. However, the traditional microwave absorbing materials cannot meet all of the requirements such as lightness, width, strength and thinness. As the microwave absorber, ferrites are favorable, because their large saturation magnetization which could lead to higher microwave permeability according to the Snoek limit [2]. Also, because of the high surface atom percentage, small size, large specific surface area and more dangling chemical bonds, ferrites might lead to multiple dielectric and magnetic resonance, having good microwave absorption performance [3–5]. But ferrite absorbers have heavier weight and lower dielectric loss which restrain them from being widely used in the field of microwave absorbing [6–8]. In order to improve the magnetic and electromagnetic absorption properties of magnetic materials, many studies have focused on new systems [9,10], such as $CoFe_2O_4$/$ZnFe_2O_4$ [11], earth-iron-boron [12] and Fe/Z type ferrite [13], etc. Among the magnetic ferrites, hard magnetic barium hexaferrite $BaFe_{12}O_{19}$ (BaM) has been widely used due to its low cost, excellent oxidation, and corrosion resistance, low density, high electrical resistivity, high saturation magnetization and large coercivity [14,15]. Simultaneously, the spinel ferrites $CoFe_2O_4$ (CFO) is a typical soft ferrite which have strong anisotropy, high saturation magnetization and moderate coercivity at room temperature [16,17]. Ferrite of calcium $CaFe_2O_4$ (CaF) is expected to be more biocompatible since calcium is inherently non-toxic. However, the single ferrite cannot meet all the requirements, the magnetic nanocomposites are of the merits of each phase. To overcome the shortcomings of the ferrites, dielectric loss fillers such as conducting polymers, carbon nanotubes and graphene are always added into the system which can obtain higher absorption and broaden the frequency band. Reduced graphene oxide (RGO), as a unique two-dimensional carbon material which is composed of sp^2-bonded carbon atoms, has received much attention due to its structure and good electrical conductivity properties [18,19] which can remedy the defect of ferrite absorbers. The integration of magnetic materials and conducing materials has attracted increased interests [20]. The composite materials have potential applications in microwave absorption because they are of not only electrical and magnetic properties [21], but also possess special electromagnetic effects generated from a synergistic effect of the components [22–24].

In the previous reports, there are few researches on the combination of three ferrites and dielectric loss fillers. In this work, (1−x)BaM/CaF/xCFO composite powders were successfully

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synthesized by the simple physically mixing of the BaM/CaF powders and CFO powders, then the (1−x)BaM/CaF/xCFO composites were deposited on the surface of graphene sheets by a deoxidation technique. The samples can obtain excellent electrical conductivity and electromagnetic properties, which obviously increases the complex permittivity of the composites and provided the material with potential microwave absorbing properties.

2. Experimental procedure

2.1. Preparation of graphite oxide (GO)

First, 2 g portion of natural flake graphite with 2 g of $NaNO_3$, and 96 mL of concentrated H_2SO_4 were mixed at 0 °C. During the following stages the mixture was continuously stirred using a magnet stirrer. 12 g of $KMnO_4$ was gradually added to the above mixture for 1.5 h. After that, the solution was transferred to a 35 °C water bath and stirred for about 2 h, forming a thick paste. Then 80 mL of distilled water was slowly dropped into the above paste and the resulting solution was stirred over a period of around 30 min while the temperature was raised to 90 °C. Finally, 200 mL of water which containing 10 mL of H_2O_2 was added for 10 min until the color of the solution turned from dark brown to yellow. The graphite oxide deposit was collected from the graphite oxide suspension by high-speed centrifugation, and repeatedly washed with distilled water until the pH = 7 and then was dried at 60 °C.

2.2. Preparation of (1−x)BaM/CaF/xCFO composite powders

BaM/CaF powders were synthesized by a one-step sol-gel method with the stoichiometric ratio of 1:2. The aqueous solution was prepared by dissolving $Ba(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2 \cdot 5H_2O$, and $C_6H_8O_7 \cdot H_2O$ into distilled water and magnetically stirred at 80 °C. Ammonia was added to the above solution to adjust the pH value to 7. The precursor was obtained by drying the mixture solution at 200 °C for 2 h, which was followed by the annealing treatment in air at 1000 °C for 4 h. The soft ferrite $CoFe_2O_4$ nano-powders were purchased from Shanghai Crystal Pure Reagent LTD commercially. (1−x)BaM/CaF/xCFO composite powders (with x = 0.2, 0.3) were obtained by ball-milling the mixtures of BaM/CaF and CFO with different mass ratios and calcined at 400 °C for 3 h.

2.3. Preparation of RGO/(1−x)BaM/CaF/xCFO composites

RGO/(1−x)BaM/CaF/xCFO composite powders were prepared with the mass ratio of 1:5. In a typical step, a certain amount of graphite oxide (GO) were dispersed in glycol by ultrasonication for 4 h. And then BaM/CaF/CFO was added and continued dispersing for 1 h. After that, the mixture was reacted at 200 °C for 24 h by a hydrothermal method. The resulting precipitate was filtrated, washed with distilled water and ethanol repeatedly and dried under vacuum at 60 °C for about 24 h.

2.4. Characterization

The phase composition of the samples was detected by an X-ray diffractometer (XRD) with Cu Kα radiation (Rigaku D/MAX-2400, Japan). The Raman spectra of the composite samples were obtained using an inVia Laser-Raman spectrometer (Renishaw Co, England) with a 514 nm radiation. The morphology of the composite powders was analyzed using a scanning electron microscope (Hitachi S-4800, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS) and the transmission electron microscopy (TEM) (FEI Tecnai G2 F20 S-TWIN, American). The thermal stabilities of the composites were analyzed by using a computerized differential thermal analysis (DTA) (STA409PC, NETZSCH, Germany) from room temperature to 650 °C in air atmosphere, with a heating rate of 10 °C/min. The magnetic hysteresis loops of the composite powders were measured by a vibrating sample magnetometer (VSM) (Lake Shore 7410, USA). The microwave absorbing properties of the material was achieved based on the coaxial transmission/reflection method. The electromagnetic parameters (ε', ε'', μ', μ'') of the samples, which were pressed to be toroidal samples with the height about 3 mm according to the mass ratio 3:1 of paraffin and composite powders, were measured using the test system composed of a vector network analyzer (VNA) (HP8720ES) and coaxial fixture.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of RGO/(1−x)BaM/CaF/xCFO composite powders with different mass ratios of BaM/CaF and CFO are shown in Fig. 1. It suggests that the three phases can coexist, the diffraction peak intensities of the each phase are dependent on their relative mass ratios and there are no any other impurity phase can be detected in the XRD patterns. The XRD patterns are consistent with $BaFe_{12}O_{19}$ phase (JCPDS 27-1029), $CaFe_2O_4$ phase (JCPDS 65-1333) and $CoFe_2O_4$ phase (JCPDS 22-1086). It can be found that the adding of graphene will not affect the crystalline structure in the reaction. So, it can be concluded that RGO/(1−x)BaM/CaF/xCFO composite powders have been obtained during the reaction process. Therefore, some other testing instruments were used to analyze the relation between graphene and BaM/CaF/CFO composite.

3.2. Raman analysis

Raman spectroscopy is also one of the most sensitive and informative techniques to characterize disorder in sp^2 carbon materials. Fig. 2 presents the Raman spectra of GO and RGO/0.8BaM/CaF/0.2CFO composite powders. There are two prominent peaks at about ~1354 cm^{-1} and ~1593 cm^{-1}, which correspond to the D and G peaks of graphene, respectively. The G band and D band arising from E_{2g} phonon of carbon sp^2 atoms and the A_{1g} phonon of carbon sp^3 atoms from defects and boundaries of lattice, respectively [25].

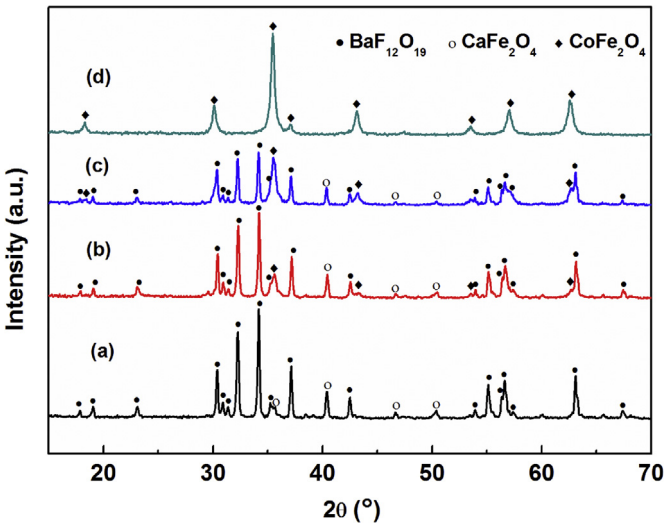

Fig. 1. XRD patterns of (a) RGO/BaM/CaF composite powders, (b) RGO/0.8BaM/CaF/0.2CFO composite powders, (c) RGO/0.7BaM/CaF/0.3CFO composite powders and (d) RGO/CFO composite powders.