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Synthesis of iron-based hexagonal microflakes for strong microwave attenuation

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ABSTRACT

Fe and Fe@SiO_2 hexagonal microflakes have been synthesized by combining a hydrothermal reaction and thermal reduction process. The phase purity, size, morphology, structure and magnetic properties of products are characterized by powder X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and vibrating sample magnetometer (VSM). The results show that the microflakes have a uniform size with the diameter around 2 μm and the thickness ranging from 150 to 200 nm and high magnetization. The microwave absorption properties of these microflakes are investigated in terms of complex permittivity and permeability. The electromagnetic measurements demonstrate that Fe@SiO_2 microflakes exhibit significantly enhanced microwave absorption performance compared to Fe microflakes, which may result from the effective complementarities between dielectric loss and magnetic loss and the improved impedance matching. The present study indicates that these Fe@SiO_2 microflakes can be promising electromagnetic wave attenuation material with strong-attenuation and broad bandwidth.

1. Introduction

With the rapid development of consumer electronics, high frequency circuit devices and radar stealth systems, the expanded electromagnetic interference has become a serious problem [1–4]. Thus, the electromagnetic wave attenuation (EMA) materials with the capability of shielding or absorbing undesired electromagnetic signals have attracted extensive attention during the last two decades. The EM wave energy can be strongly attenuated by this kind of material and dissipated into heat through magnetic losses and dielectric losses if the input characteristic impedance of the material is matched with that of the space. Till now, the most widely used EMA materials include ferrites [5–7], conducting fibers [8], magnetic metal and alloys [9,10], and carbon nanotubes [11,12], etc. Among all these potential EMA candidates, fine magnetic metal particles (e.g. carbonyl iron and iron-based powders) have been especially focused on because they show the high Curie temperature and high relative complex permeability in the gigahertz range due to their high saturation magnetization which can be used to make thinner EMA [13]. However, for practical EMA applications, the magnetic metals have to be used as fine particles dispersed in an insulating matrix and the effective microwave properties of the composites are mainly depended on both the intrinsic magnetic characteristics of the bulk materials and other parameters including particle size, shape and microstructure [14,15]. Moreover, the initial permeability of the composite μ'_0 can be theoretically obtained from Eq. (1) according to the Maxwell-Garnett mixing law and Eq. (1) can be further simplified and approximately expressed by Eq. (2) [16],

$$\mu'_0 = \frac{(\mu_b - 1)p}{(\mu_b - 1)(1-p)N_d + 1} + 1 \quad (1)$$

$$\mu'_0 \approx \frac{p}{(1-p)N_d} + 1 \quad (2)$$

where μ_b is the permeability of the corresponding bulk material, p is the volume concentration of fillers, and N_d is the demagnetizing factor. From the above equations, it is found that the permeability of

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EMA composites is closely related to the demagnetizing factor (N_d), which is mainly determined by the shape of the particles. Furthermore, it is also clearly shown that the μ'_0 of EMA composites filled with the conventional spherical particles is rather small, which is an intrinsic drawback for the conventional spherical fillers. To overcome this drawback and greatly increase the permeability for the EMA composites, one effective way is to make the fillers into flake-like shape which has the much smaller N_d [17].

On the other hand, in order to decrease the eddy current loss at the high frequency, the metal particles prefer to be small and the thickness of flake-like fillers should be lower than 1 μm.In the previous report, the magnetic metal flakes are usually obtained by mechanical grinding of their precursors. However, the particle size distribution for the flakes prepared by this method is quite wide and the thickness of the flakes also cannot be exactly controlled. Currently, the hydrothermal method has been widely employed for synthesis of many different kinds of materials. During the hydrothermal process, the morphology and composition of the particles can also be exactly controlled by the tuning the experimental parameters [18,19]. In this study, we have developed a simple two-step process to synthesize magnetic iron-based microflakes with thickness around a few tens nanometers. Firstly, iron oxide (α-Fe_2O_3) microflakes were fabricated via a facile one-pot hydrothermal route. Secondly, the as-prepared oxide microflakes were converted into metal microflakes via a hydrogen-thermal reduction process. Nevertheless, metallic particles are easily oxidized in the atmosphere environment and they have poor impedance matching between the materials and the free space caused by the high conductive value, which may worsen their attenuation properties [20,21]. To address this concern, the α-Fe_2O_3 microflakes samples were further coated with a SiO_2 insulating layer and then Fe@SiO_2 flakes could be gained after the hydrogen-thermal reduction. The flake-like ferromagnetic metal particles prepared by this method exhibit a uniform size and hexagonal shape and have a high aspect ratio. The structures, morphologies, static magnetic and electromagnetic properties of these flake-like magnetic metal particles were investigated. It is expected that the as-prepared hexagonal iron-based microflakes would be ideal candidate for EMA materials.

2. Experimental section

2.1. Synthesis of α-Fe_2O_3 microflakes

All reagents including iron chloride ($FeCl_3 \cdot 6H_2O$), magnesium chloride ($MgCl_2 \cdot 6H_2O$), sodium hydroxide (NaOH) and sodium silicate solution ($Na_2Si_3O_7$, Na_2O ~ 10.6%, SiO_2 ~ 26.5%) were purchased from Sigma-Aldrich and were used without further purification. The α-Fe_2O_3 microflakes were synthesized by a simple hydrothermal method. In a typical process, 2.703 g $FeCl_3 \cdot 6H_2O$ and 0.051 g $MgCl_2 \cdot 6H_2O$ were dissolved in 30 ml distilled water with magnetic stirring. Subsequently, 0.041 ml $Na_2Si_3O_7$ solution was added drop by drop to the above solution, followed by the addition of 5.2 g NaOH. Then the mixture was stirred vigorously for 30 min and a brown precipitate appeared. The resultant solution had a pH value of around 14. The obtained solution was sealed in a Teflon-lined stainless steel autoclave, which was kept at 200 °C for 4 h in an electric oven. After the reaction, the autoclave was cooled to ambient temperature and the products were obtained by centrifugation and washing several times with distilled water and ethyl alcohol to remove the remaining surfactants. Finally, the products could be obtained after being dried in a vacuum oven at 60 °C for 2 h.

2.2. Synthesis of Fe and Fe@SiO_2 microflakes

The flake-like Fe particles were prepared by a hydrogen-thermal reduction reaction. In a typical process, 2 g of as-prepared α-Fe_2O_3 microflakes were reduced in a pure H_2 atmosphere at 600 °C for 4 h. Then the reduced products were cooled in H_2 atmosphere to room temperature naturally in the furnace. The colour of the samples was changed from red to dark sliver after the reduction process. For the preparation of Fe@SiO_2 microflakes, the α-Fe_2O_3 flake samples were first coated with a SiO_2 insulating layer through a modified Stöber process. In a typical coating process, α-Fe_2O_3 microflakes (1 g) were first dispersed in ethanol (250 ml) and ultrasonicated in order to break down agglomerates. In the next step, ammonium hydroxide solution (3 ml, 28%) and 1 ml of TEOS were added to the mixture to initiate the deposition of silica shells on the α-Fe_2O_3 microflakes. After that, the suspension was mechanical stirred at 300 rpm for 2 h to complete the reaction at room temperature. The α-Fe_2O_3/SiO_2 particles were then washed with ethanol two times and then dried at 60 °C for 1 h in a vacuum oven. Last, the Fe@SiO_2 flakes could be gained after the hydrogen-thermal reduction with the same condition to the synthesis of Fe microflakes.

2.3. Characterizations

X-ray diffraction (XRD) patterns of the samples were obtained with a Rigaku Ultima IV diffractometer with a Cu Kα source ($\lambda = 0.154056$ nm). The particle size and morphology of the prepared samples were observed using a JOEL JSM 6701F field emission scanning electron microscope (FESEM) at an accelerating voltage of 20 kV. Static magnetic properties of as-synthesized Fe and Fe@SiO_2 microflakes were measured by using a vibrating sample magnetometer (VSM, ADE Magnetics EV-9). For microwave absorption measurements, silicon resin-based composites were prepared by homogeneously mixing certain weight percentage of the prepared Fe and Fe@SiO_2 microflakes with silicon resin and pressed into toroidal-shaped samples with an outer diameter of 7.00 mm and an inner diameter of 3.04 mm. Complex permeability and permittivity of the composites were measured by using an Agilent VNA (Vector Network Analyzer) N5232A with a reflection-through-line calibration, over 1–18 GHz, using a set of 7 mm coaxial air-line with length of 49.96 mm. The reflection loss (RL) of the composites was estimated from their complex permittivity ($\varepsilon_r = \varepsilon'_r - j\varepsilon''_r$) and permeability ($\mu_r = \mu'_r - j\mu''_r$) at a given frequency and thickness layer according to the transmit line theory, which can be expressed as the following equations [22,23]:

$$Z_{in} = Z_0(\mu_r/\varepsilon_r)^{1/2} \tanh\left[j(2\pi ft/c)(\mu_r\varepsilon_r)^{1/2}\right] \quad (3)$$

$$\mathrm{RL(dB)} = 20\log|(Z_{in} - Z_0)/(Z_{in} + Z_0)| \quad (4)$$

where Z_{in} is impedance of the composites backed by a ground plane, Z_0 is the intrinsic impedance of free space, c is the velocity of light in free space, t is thickness of the attenuation material, f is the frequency of the incident EM wave.

3. Results and discussion

The crystalline structure of the prepared product was studied by the X-ray diffraction (XRD) as shown in Fig. 1. Fig. 1a shows the XRD pattern of the as-prepared α-Fe_2O_3 microflakes. All the diffraction peaks can be indexed to the rhombohedral α-Fe_2O_3 (hematite) phase without the presence of other diffraction peaks from any impurities. The strong and sharp diffraction peaks indicate that as-synthesized α-Fe_2O_3 microflakes were well-crystallized. Fig. 1b