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Synthesis, characterization and microwave absorption properties of polyaniline/Sm-doped strontium ferrite nanocomposite

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ABSTRACT

Sm-doped strontium ferrite nanopowders ($SrSm_{0.3}Fe_{11.7}O_{19}$) and their composites of polyaniline (PANI)/$SrSm_{0.3}Fe_{11.7}O_{19}$ with 10 wt% and 20 wt% ferrite were prepared by a sol–gel method and an in-situ polymerization process, respectively. The structure, magnetic properties and microwave absorption properties of the samples were characterized by means of X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), transmission electron microscope (TEM), vibrating sample magnetometer (VSM) and vector network analyzer, respectively. The particle size of $SrSm_{0.3}Fe_{11.7}O_{19}$ was about 35 nm by using XRD. The ferrite successfully packed by PANI. PANI/$SrSm_{0.3}Fe_{11.7}O_{19}$ possessed the best absorption property with the optimum matching thickness of 3 mm in the frequency of 2–18 GHz. The value of the maximum reflection loss (RL) were −26.0 dB at 14.2 GHz with the 6.5 GHz bandwidth and −24.0 dB at 13.8 GHz with the 7.9 GHz bandwidth for the samples with 10 wt% and 20 wt% ferrite, respectively.

1. Introduction

In recent decades, electromagnetic waves in the GHz range are being increasingly used in wireless communication tools, local area networks, healthcare and defense sectors and other communication equipment. Unfortunately, the increasing usage of electromagnetic wave devices results in serious electromagnetic interference (EMI) [1]. To solve the EMI problem, considerable interest has been attracted to electromagnetic wave absorber with strong absorption, wide absorption bandwidths, low density, and good thermal stability. The conventional hexagonal ferrites such as strontium ferrites do not function well in microwave range due to the high anisotropy field of H_A. Many researchers have reported that the H_A of hexagonal ferrite can be changed by using rare earth (RE) ion substituting Fe^{3+} such as La^{3+} [2–4], Pr^{3+} [3], Eu^{3+} [5], Nd^{3+} [6], etc [7–9], resulting in not only a shift in resonance frequency but also a remarkable improvement of magnetic loss in the GHz frequency. Because the RE ions have unpaired 4*f* electrons, the occurrence of 4f-3d couplings of the angular momentum which improve the electromagnetic properties. Moreover, 4f shell of rare earth ions is shielded by $5s^25p^6$ and almost not affected by the potential field of surrounding ions leading to the enhancement of the coupling [3,4]. However the single magnetic loss can not bring about ideal consequence of the microwave absorption because that it can only absorb electromagnetic waves generated by magnetic sources while it does not work to electromagnetic waves produced by an electric source, and the high density of the hexagonal ferrite is a big problem limiting its application. A good way to overcome these problems is a combination of the strontium ferrite with the conductive polymer. Compared with the traditional ferrite materials, conducting polymers such as polyaniline (PANI) own advantages of low density and high complex permittivity values [6], which not only improves the dielectric loss of ferrite/conductive polymer composite but also reduces its density. The composites of PANI wrapped ferrite provide a promising further of absorption material which can absorb the microwave both generated by electric and magnetic source.

Recently, considerable efforts have been made towards the development of preparation conducting polymer/ferrite composite. S.P. Gairola et al. prepared polyaniline (PANI) nanocomposite with $Mn_{0.2}Ni_{0.2}Zn_{0.4}Fe_2O_4$ ferrite by mechanical blending, and they reported the composite of 2.5 nm thickness with 20%wt PANI showed strong microwave absorption in 8–12 GHz (X-band) [10]. Tzu-Hao Ting et al. synthesized PANI/$BaFe_{12}O_9$ composite by in situ polymerization at different aniline/Ba ferrite weigh ration (Ani/Ba ferrite = 1:2, 1:1 and 2:1). Their results indicated that the microwave absorption properties can be modulated simply by controlling the content of PANI on the samples for the required frequency

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bands [11]. Azadeh Tadjarodi et al. reported an extension in chemical free surfactant methods to synthesize the PANI nanocomposites with the magnetic core of $Ba_{0.69}Cr_{0.17}Cd_{0.07}Zn_{0.7}Fe_{12}O_{19}$. As a result of this research, the products showed the maximum reflection loss of −16 dB with 2.1 mm thickness of the composites [12]. Xin Tang et al. also studies the PANI-coated M-type $BaFe_{12}O_{19}$ ferrite composites, and they found that the interaction and interfacial polarization were seen as important factors contributing to the influence on microwave absorption of the composite [13]. PANI/$BaFe_{12}O_{19}$/$Ni_{0.8}Zn_{0.2}Fe_2O_4$ nanocomposite was prepared by Ying Huang et al., and the maximum reflection loss is −19.7 dB at 7.3 GHz [14]. Liangchao Li et al. prepared the Sm-substituted LiNi ferrite (Sm:Li = 0.8:1) by a novel rheological phase reaction method, and $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$/PANI nanocomposite was synthesized by an in situ polymerization in aqueous in the presence of $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ [15]. Their group also reported the core–shell structure of $Zn_{0.6}Cu_{0.4}Cr_{0.5}Fe_{1.46}Sm_{0.04}O_4$/PANI composite which the nanosized $Zn_{0.6}Cu_{0.4}Cr_{0.5}Fe_{1.46}Sm_{0.04}O_4$ ferrite doped with Sm as magnetic core and PANI as conducting shell. When the content of $Zn_{0.6}Cu_{0.4}Cr_{0.5}Fe_{1.46}Sm_{0.04}O_4$ in composite approximately 20 wt%, the maximum reflection loss of −22.46 dB appeared at approximately 14.7 GHz [16]. While the composite of polyaniline/Sm-doped strontium ferrite nanoparticles has been reported rarely.

In our previous work, we have reveals the RE-doped strontium ferrite ($SrRE_xFe_{12-x}O_{19}$, $0 \le x \le 0.5$) obtains enhancing magnetic properties, and when $x = 0.3$, the ferrite behaves the best magnetic properties without changing the phase of hexagonal structure of strontium ferrite [17]. Therefore, in this paper, we motivated to synthesize Sm-doped strontium ferrite nanopowder ($SrSm_{0.3}Fe_{11.7}O_{19}$) by sol–gel method, and PANI/$SrSm_{0.3}Fe_{11.7}O_{19}$ nanocomposite was prepared by in-situ polymerization method, respectively. The influences of PANI on the structure and the behavior of magnetic and absorption properties of $SrSm_{0.3}Fe_{11.7}O_{19}$ at room temperature are discussed.

2. Experimental

2.1. Preparation of the samples

2.1.1. Materials

Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98.5% purity), strontium nitrate ($Sr(NO_3)_2$, 99.5% purity), aniline (An, 99.5% purity), hydrochloric acid (HCl, 36%~38% purity) and ammonium persulfate (APS, 98.0% purity) were all provided by the Sinopharm Chemical Reagent Co., Ltd. Citric acid ($C_6H_8O_7$, 99.5% purity), and ammonia solution ($NH_3 \cdot H_2O$, 25% purity) were received from Jiangsu Tongsheng Chemical Regent Co., Ltd. Samarium nitrate ($Sm(NO_3)_3 \cdot 6H_2O$, 99.9% purity) was purchased from Aldrich. All of the chemical reagents were used without further purification.

2.1.2. Preparation of Sm-doped strontium ferrite nanoparticles

Stoichiometric amounts of $Sm(NO_3)_3$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Sr(NO_3)_2$ were dissolved in a minimum amount of deionized H_2O by stirring at 40 °C with Fe/Sr ratio of 10.5. Citric acid was then added to the mixture solution to chelate these ions. The molar ratio of citric acid to metal ions of Sr^{2+} and Fe^{3+} was 1.5:1. Ammonia was added to adjust the pH value to 7. The clear solution was slowly evaporated at 70 °C under constant stirring, forming a viscous gel. By increasing the temperature up to 200 °C, the gel precursors were combusted to form loose powders. Finally, the obtained powder was calcined in air at 900 °C for 2 h in a muffle oven. The $SrSm_{0.3}Fe_{11.7}O_{19}$ particles were thus obtained.

2.1.3. Preparation of PANI/$SrSm_{0.3}Fe_{11.7}O_{19}$ nanocomposite

1 ml aniline monomer and $SrSm_{0.3}Fe_{11.7}O_{19}$ (account for 10 wt% and 20 wt% of aniline quantity) were added in 35 ml hydrochloric acid solution (0.1 mol L^{-1}) and dispersed by ultrasonic wave for 30 min. 2.49 g of ammonium persulfate was a dissolved in 15 ml hydrochloric acid solution (1 mol L^{-1}). The ammonium persulfate solution was then slowly added dropwise to the above mixture solution with vigorous stirring. The polymerization was carried out for 12 h. The composites were obtained by filtering and washing the reaction mixture with deionized water and ethanol and dried under vacuum at 60 °C for 24 h. PANI/$SrSm_{0.3}Fe_{11.7}O_{19}$ nanocomposite was thus synthesized.

2.2. Characterization

The resulting powder was characterized by X-ray powder diffraction (XRD) using a diffractometer (RIGAKU, model D/max) with CuKα radiation of wavelength $\lambda = 0.15418$ nm. Its morphology was studied with a transmission electron microscope (JEOL, model JEM 2001). Fourier transform infrared spectroscopy (FT-IR) for the prepared samples were carried out using the infrared spectrophotometer (NICOLET, model NEXUS 670) in the range from 2500 to 400 cm^{-1} with a resolution of 1 cm^{-1}. Magnetization measurements were taken at room temperature (293 K) using a vibrating sample magnetometer (LDJ, model 9600-1). The complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) of the samples were measured by a microwave vector network analyzer (AGILENT, model N5244A) in the frequency range 2–18 GHz by using coaxial reflection/transmission technique (where the ε', ε'', μ' and μ'' is measured and the dielectric loss angle tangent ($\tan\delta_\varepsilon = \varepsilon''/\varepsilon'$) and the magnetic loss angle tangent ($\tan\delta_\mu = \mu''/\mu'$) were calculated by the measured parameters.). The samples for vector network analyzer were pressed to be toroidal samples with OD 7 mm, ID 3.04 mm and height about 3 mm according to the mass ration 1:1 of between paraffin and PANI/$SrSm_{0.3}Fe_{11.7}O_{19}$ nanocomposite. Microwave absorption properties were evaluated by the reflection loss (RL), which was derived from the following formulas [18]:

$$z_{in} = z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[j\frac{2\pi fd}{c}\sqrt{\mu_r\varepsilon_r}\right] \quad (1)$$

$$RL = 20\log\left|\frac{z_{in} - z_0}{z_{in} + z_0}\right| \quad (2)$$

where f is the frequency of incident electromagnetic wave, d is the absorber thickness, c is the velocity of light, Z_0 is the impedance of free space, and Z_{in} is the input impedance of absorber. The best absorbing properties is described by the impedance matching condition when $Z_0 = Z_{in}$. The −10 dB absorbing bandwidth means that the frequency bandwidth can achieve 90% of reflection loss.

3. Results and discussion

3.1. Phase structure and composition analysis

3.1.1. Polymerization

It is known to us that the surface charge of metal oxide is positive below the pH of the point of zero charge (PZC), while it becomes negative above PZC. Since the surface of magnetite has PZC of pH = 6 [19], it is positive charged in 0.1 mol L^{-1} hydrochloric acid solution which the value of pH is above 6. Therefore, cl^- is absorbed and compensates the positive charge on ferrite. In this approach, aniline monomers are converted to cationic anilinium ions in acidic conditions. Thus, the electrostatic interactions occur between