Journal of Magnetism and Magnetic Materials 330 (2013) 163–168

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

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

The role of multi-walled carbon nanotubes on the magnetic and reflection loss characteristics of substituted strontium ferrite nanoparticles

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ARTICLE INFO

Article history:
Received 1 April 2012
Received in revised form
15 October 2012
Available online 9 November 2012

Keywords:
Ferrite
Magnetic property

ABSTRACT

Substituted strontium ferrite $SrFe_{12-x}(Ni_{0.5}Mn_{0.5}Zr)_{x/2}O_{19}$/multi-walled carbon nanotubes (MWCNTs) composites were prepared by a sol–gel method. X-ray diffraction patterns confirm the formation of single phase ferrite nanoparticle and nanocomposites of ferrite/carbon nanotubes. Fourier transform infrared spectroscopy demonstrates the existence of functional groups on the surface of carbon nanotubes. Superconducting quantum interference device measurements showed that the values of specific saturation magnetization increases, while coercivity decreases with an increase in substitution content. Zero field cooled magnetization and field cooled magnetization curves display that with an increase in substitution content, the blocking temperature increases. Field emission scanning electron microscopy micrographs demonstrate that ferrite nanoparticles were attached on external surfaces of the carbon nanotubes. The investigation of the microwave absorption indicates that with an addition of carbon nanotubes, the real and imaginary parts of permittivity and reflection loss enhanced. It is found that with increasing the thickness of absorbers, the resonance frequencies shift to lower regime.

1. Introduction

Recently, the number of communication devices that utilize gigahertz range microwave radiation has increased. However, electromagnetic interference (EMI) is a matter of crucial concern in high frequency electronic devices [1,2]. Special electromagnetic materials are often used in high-speed electronic circuits to reduce the electromagnetic radiations, decrease the noise level of signals, and ensure the electromagnetic compatibility. One promising technique to prevent EMI is the use of microwave absorption materials [1]. Carbon nanotube in polymer matrix is considered a suitable composite for microwave applications because of high dielectric loss, electromagnetic interference shielding, and microwave absorbing media [3,4]. To optimize the potential applications of CNTs, it is required to fabricate their composite with other materials.

There are several literatures regarding the formation of ferrite-MWCNTs nanocomposites including zinc ferrite/CNTs, Mn–Zn ferrite/CNTs, cobalt ferrite/CNTs and strontium ferrite/carbon nanotubes [5–8]. Cobalt ferrite beads decorated CNTs were also synthesized through an improved co-precipitation technique [9]. The TEM micrographs demonstrated very beautiful array of cobalt ferrite with average diameter of 10 nm. A magnetic MWCNTs-based composite, MWCNTs/NiZnFeO, was also synthesized via a facile solvothermal approach [10].

Considering the outstanding properties of CNTs as well as strontium ferrite nanoparticles, strontium ferrite/CNTs nanocomposites would be very attractive for practical applications. Strontium ferrite/CNTs can be used in the fabrication of high frequency microwave absorbing nanocomposite, and various microwave and radar devices due to its high permeability and permittivity losses. Recent works proved that magnetic nanoparticles could be fabricated using carbon nanotubes as an inhibition template.

In recent years our research group has proposed several new microwave absorbing materials [11–14]. In the present work, nanocomposite of ferrite/carbon nanotubes were synthesized. The structural, magnetic and reflection loss characteristics of prepared nanocomposites were evaluated. Reflection loss evaluations indicate that the nanocomposites display a great potential application as wide-band electromagnetic wave absorbers. It is found that microwave absorbing bandwidth is simply modulated by manipulating the thickness of nanocomposites.

2. Experimental

The preparation of nanocomposite has been done in three stages. In the first stage, in order to synthesize $SrFe_{12-x}(Ni_{0.5}Mn_{0.5}Zr)_{x/2}O_{19}$ ferrite nanoparticles, solutions were prepared by a sol–gel process. A stoichiometric amounts of $Fe(NO_3)_3\cdot 9H_2O$, $Sr(NO_3)_2$, $Ni(NO_3)_2\cdot 6H_2O$, $Mn(NO_3)_2\cdot 4H_2O$ and $ZrCl_4$ were dissolved in distilled water. Then citric acid (weighed as the citric acid/metal ion molar ratio of 1:1) was added into the above

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http://dx.doi.org/10.1016/j.jmmm.2012.10.033

mixture. This solution was slowly evaporated at 80 °C until a high viscous residual was formed and then the viscous residue was heated at 200 °C to get dried gel. Before annealing, the gel was preheated to 400 °C for 1 h to decompose the organic precursor. Finally, the dried gel was sintered at 800 °C for 1 h. In the second step, the pristine MWCNTs were dispersed into concentrated nitric acid with constant stirring. Then, the black solution was treated with ultrasonicator for 1 h. Afterwards, it was dried at 200 °C. In the third step, 3 g poly(acrylic acid) (PAA) was dissolved in distilled water. Then MWCNTs were dispersed in this solution by employing ultrasonic for 30 min. Substituted strontium ferrite nanoparticles were added to the above solution and dispersed with sonication process for 1 h. The MWCNTs were added with 2 vol%, 4 vol%, 6 vol % and 8 vol % to SrM solution in order to evaluate the effect of MWCNTs fraction on magnetic and microwave properties of nanocomposites. Then the solution was heated under constant stirring at 60 °C. Finally nanocomposites were annealed at 500 °C in argon atmosphere for 1 h.

The phase identification was carried out by X-ray diffraction (XRD) with employing Cu $K\alpha$. FTIR spectroscopy was used to study chemical structure variation and to identify the functional groups on the outer surface of carbon nanotubes. FE-SEM was used to evaluate morphologies of composites. The magnetic properties were measured at 2 K using a superconducting quantum interference device (SQUID). The blocking temperature of nanocomposites was also measured by means of ZFC–FC curves. Microwave properties of the composites were measured using a vector network analyzer in the 8–12 GHz. The composite specimens for reflection loss measurements were fabricated by mixing of nanocomposite and PVC powder in the mass ratio of 80:20. The pressed composites were in the cylindrical form with the thicknesses of 1.5–1.8 mm in a step of 0.1 mm and the diameter of 40 mm. The complex scattering parameters that correspond to the reflection (S_{11} or S_{22}) and transmission (S_{21} or S_{12}) in the composite samples were measured using a vector network analyzer. Full two port calibrations were initially done on the test setup in order to remove errors due to the directivity, source match, load match, isolation, etc., in both the forward and reverse directions. The complex permittivity was determined from the measured scattering parameters using Agilent software module 85071.

3. Results and discussion

3.1. Structural analysis of composites

Fig. 1 displays the XRD patterns of synthesized nanocomposites with composition of x=2.5. The XRD patterns of corresponding strontium ferrite nanoparticles (x=2.5) was also included to confirm the presence of well consistence of peaks. The peak at 26.6 deg. in pattern of nanocomposite is attributed to the graphite (002) lattice plane of the MWCNTs. The existence of graphite lattice plane in XRD pattern indicates that the nanocomposites are successfully synthesized by incorporation of carbon nanotubes into the solution of strontium ferrite. It is found that there is no secondary phase in the ferrite nanoparticles and nanocomposites. Since the ferrite particles were sintered at relatively high temperature, the absence of any kind of secondary phases was almost predicted.

FTIR spectroscopy is a very informative measurement for studying the functional groups attached to side wall of MWCNTs. Fig. 2 displays the infrared spectra of acid-pretreated MWCNTs, and acid pretreated PAA-carbon nanotubes. It is well-known that treating the MWCNTs with nitric acid could create considerable functional groups such as carboxyl on outer surface of MWCNTs.

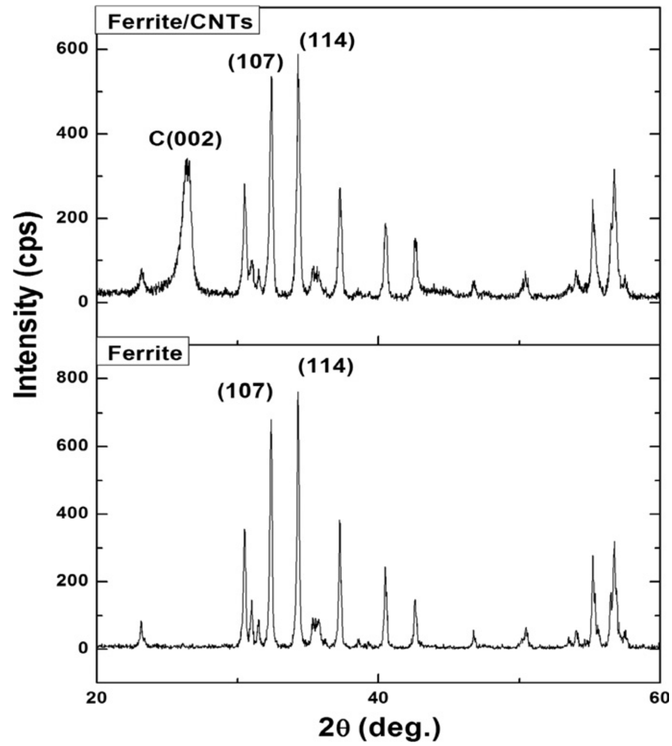

Fig. 1. XRD patterns of Ni–Mn–Zr substituted strontium ferrite nanoparticles (x=2.5) and nanocomposites of ferrite (x=2.5)-multi-walled carbon nanotubes (8 vol%).

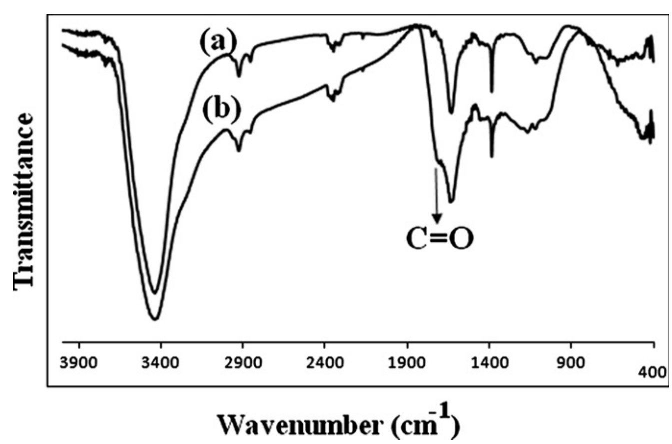

Fig. 2. FTIR spectra of: (a) acid-pretreated MWCNTs; (b) acid pretreated PAA-carbon nanotubes.

Poly(acrylicacid) covalently grafted MWCNTs (PAA-g-MWNTs) prepared through the ‘fishing’ process, containing many of carboxyl groups (–COOH) on the outer surface of MWCNTs. The MWCNTs act as “fishhooks”, and the “living” polymer radicals are “fish”, which are enthalpically favored to absorb onto the surface of MWCNTs and continue to propagate until all the active sites are consumed [15]. The peaks in the 2800–3000 cm^{-1} region are characteristics of C–H stretching. The peak at 1730 cm^{-1} in Fig. 2(b) can be assigned to the stretching mode of carbonyl groups (C=O), indicating the presence of PAA chains in PAA-carbon nanotubes [16]. In addition the bands at 3434 and 1630 cm^{-1} are corresponding to the O–H stretching modes. The band at 1384 cm^{-1} is ascribed to asymmetric NO_3^- stretching vibration arising from the residual nitrate groups originating from the precursors.