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Influence of carbon nanotubes on structural, magnetic and electromagnetic characteristics of Mn–Mg–Ti–Zr substituted barium hexaferrite nanoparticles

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ABSTRACT

In this research work, magnetic nanocomposites of multiwalled carbon nanotubes (MWCNTs) decorated with substituted barium hexaferrite nanoparticles with composition of $BaFe_{12-x}(MnMgTiZr)_{x/4}O_{19}$ ($x = 0$ –2.5 in a step of $x = 0.5$) have been synthesized by a co-precipitation technique. The structural, magnetic and microwave absorption properties of samples were investigated by X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscope (FESEM), vibrating sample magnetometer (VSM) and vector network analyzer (VNA). The XRD and FTIR results indicated that the nanocomposites were synthesized successfully. FESEM micrographs demonstrated that the ferrite nanoparticles were attached to the external surfaces of the carbon nanotubes. The results of hysteresis loops revealed that with adding MWCNTs to the ferrite nanoparticles, the saturation magnetization and coercivity of samples are decreased. The vector network analysis results showed that the highest value of reflection loss of nanocomposite was −42.91 dB at 16.77 GHz with an absorption bandwidth of more than of 4 GHz. The obtained results reflected that the proposed nanocomposites could be introduced as electromagnetic wave absorption materials for microwave device applications.

1. Introduction

The rapid development of gigahertz (GHz) electronic systems, telecommunications and wireless communications have resulted in increasing electromagnetic interference (EMI) [1]. So there is a lot of interest in electromagnetic-absorber technology in recent years. Electromagnetic wave absorbers with the capability of absorbing unwanted electromagnetic signals are used to suppress electromagnetic noise and avoid electromagnetic interference in electronic devices. Among the various microwave absorbers, the M-type hexagonal ferrites are special kinds of absorbing materials due to their magnetic losses in GHz rang. Barium ferrite powders are ideal fillers for the development of electromagnetic attenuation materials at microwave due to their low cost, low density, high stability, large electrical resistivity and high microwave magnetic loss [2–4]. It is well known that the electrical and magnetic properties of ferrites are strongly influenced by their composition and can be improved by the substitution for Fe^{3+} with other ions. Suitable materials to considered as EM wave absorbers should be owned the excellent dielectric loss and magnetic loss. However, $BaFe_{12}O_{19}$ posses poor dielectric loss and fairly strong magnetic loss, which is resulted in poor matching of dielectric loss and magnetic loss [5]. So it indicates the poor microwave absorbing properties [6]. Therefore, much effort has been carried out to improve the electromagnetic properties of $BaFe_{12}O_{19}$ [7]. These days the composite materials developed by adding conductive filler into the magnetic materials with their adjustable electromagnetic performance can be a potential candidate for microwave applications [8]. The special structure, high aspect ratio, low density and remarkable electrical properties of carbon nanotubes (CNTs) make them an excellent conductive filler to create conductive composites at very low filling concentration [9]. The unique mechanical, electrical and magnetic properties of CNTs have attracted considerable attention in wide application. The small size effect, quantum size effect and macroscopic quantum tunneling effect of CNTs lead to cooperation effects which make the energy range of microwave after electronic level splitting. The high specific surface area and a large number of surface suspension parts of CNTs lead to interfacial polarization and multiple scattering and therefore enhance their

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absorbing properties [10]. Prominent microwave properties of CNTs as well as barium ferrite nanoparticles cause the high permeability and permittivity losses of BaM/CNTs nanocomposites [11]. So barium ferrite/CNTs nanocomposites are predicted to be used in the fabrication of high frequency microwave absorbing nanocomposite and various microwave and radar devices.

In this article, substituted barium ferrite particles were firstly synthesized by a co-precipitation technique and then the substituted barium ferrite (BaM)/multiwalled carbon nanotubes (MWCNTs) nanocomposites were prepared under mechanical stirring after the ultrasonic dispersion of the mixture. Through the combination, we obtained substituted Ba-hexaferrite/MWCNTs nanocomposite with excellent magnetic and electromagnetic properties. Structure, morphology and magnetic properties of nanocomposite materials were characterized by various instruments and investigated.

2. Materials and methods

The ferrite/MWCNTs nanocomposites have been prepared in two steps. In the first step, the substituted Ba-hexaferrite nanoparticles with nominal composition of $BaFe_{12-x}(MnMgTiZr)_{x/4}O_{19}$ (x = 0, 0.5, 1, 1.5, 2, 2.5) were synthesized by a co-precipitation technique. $FeCl_3$(Merck,>98%), $BaCl_2.2H_2O$(Merck,>99%), $MnCl_2.4H_2O$(Merck,>98%), $MgCl_2.6H_2O$(Merck,>98%), $TiCl_4$(-Merck,>98%), $ZrCl_4$(Merck,>98%), and NaOH were used as the starting materials. Stoichiometric amounts of the salts were dissolved in sufficient deionized water and stirred to achieve an aqueous solution. Subsequently, NaOH solution (1 M) was gradually added to the above solution while stirring to form the desirable precipitates. The pH value of the solution was adjusted to 12. Then, the precipitates were filtered and washed with distilled water for several times until pH value reached neutral. Afterward, the precipitates were dried at 70 °C. Finally, the dried precipitates were calcined at 900 °C for 2 h. In the second step, the multiwalled carbon nanotubes (>98%, ID = 5–15 μm, OD~ 50 nm) were activated by a chemical function technique. In this way, MWCNTs were sonicated in a solution of concentrated nitric acid for 2 h. Then functionalized MWCNTs were washed with distilled water for several times until pH value reaches natural and then dried at 80 °C. In order to preparation of the ferrite/MWCNTs nanocomposites, the functionalized MWCNTs have sonicated in 100 mL deionized water to disperse completely. Subsequently, MWCNT solution was dripped to substituted Ba-hexaferrite solution and sonicated for 2 h. The volume percentage of MWCNTs in nanocomposite samples were 10%. Finally, the nanocomposites were dried at 70 °C for 2 h.

The crystal structures of the nanocomposites were determined by X-ray diffraction on a Philips diffractometer using Cu-Kα radiation. The Fourier transform infrared (FTIR) spectra of the nanocomposite samples were obtained using (Nicolet 100IR) Fourier transform spectrometer in the range of 400–4000 cm^{-1}. Field emission scanning electron microscopy (FESEM) (JSM-7000F.JEOL) was employed to study of the surface morphology of the nanocomposites. The magnetic properties of the samples were investigated by vibrating sample magnetometer (VSM) (7400 Lake Shore) with a maximum field strength of 20 kOe. Variation of the reflection loss in (dB) versus frequency was measured using a vector network analyzer (VNA) (R&S-ZVK) from 8 to 12 GHz. All measurements were performed at room temperature.

3. Results and discussion

3.1. Microstructure characteristics

The phase identification of the prepared nanocomposites was carried out with XRD patterns. Fig. 1 shows the XRD patterns of MWCNTs, ferrite nanoparticles, and ferrite/MWCNTs nanocomposites. It is observed that the diffraction peaks at 2θ = 30.29°, 30.80°, 32.14°, 34.09°, 37.04°, 40.27° and 42.38° can be assigned to (110), (008), (107), (114), (203), (205) and (206) respectively, which match well with the typical hexagonal planes of the standard pattern of $BaFe_{12}O_{19}$ (ICSD 00-039-1433) and no obvious peaks from secondary phases were observed. The diffraction peak which appeared at 26.4° revealing MWCNT plane of (002), indicated that the MWCNT structure was not destroyed through functionalization and compositing processing. Additionally, it can be observed that the diffraction peaks relating to MWCNTs and substituted $BaFe_{12}O_{19}$ were appeared together in Ba-hexaferrite/MWCNTs nanocomposites, indicating that the nanocomposites were synthesized successfully. The average crystallite size of the substituted barium ferrite was calculated using the Scherrer's formula [12]:

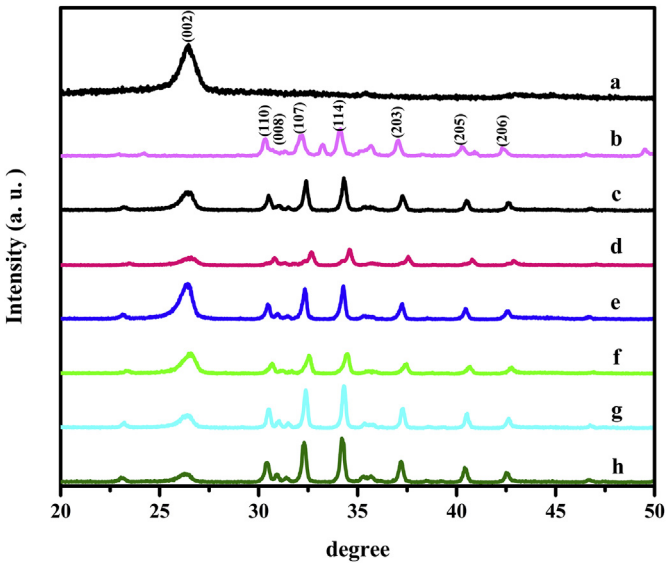

Fig. 1. XRD pattern of (a) functionalized MWCNTs, (b) $BaFe_{10}(MnMgTiZr)_{1/2}O_{19}$ nanoparticles and $BaFe_{12-x}(MnMgTiZr)_{x/4}O_{19}$/MWCNTs nanocomposites with (c) x = 0, (d) x = 0.5, (e) x = 1, (f) x = 1.5, (g) x = 2, (h) x = 2.5.

$$D = 0.9\lambda/\beta \cos\theta \quad (1)$$

Where D is the crystallite size, λ is the radiation wavelength (0.154 nm for CuKα), β is the full width of half maximum in (2θ), and θ is the diffraction peak angle. The crystallite size of nanoparticles lies in the range of 26–31 nm.

FTIR spectroscopy is a very informative measurement for identifying the nature of chemical bands of pure and nanocomposite samples and characterizing the functional groups attached to the sidewall of MWCNTs. The FTIR spectrograms of samples are shown in Fig. 2 to identify the nature of chemical bonds of functionalized MWCNTs, ferrite particles, and ferrite/MWCNTs nanocomposite. The obvious characteristics absorption peaks of $BaFe_{12}O_{19}$ at 573 cm^{-1} and 427 cm^{-1} associated with the asymmetric stretching vibrations of the octahedral and tetrahedral sites [13], can be seen at FTIR spectra curve of ferrite particles. The position of Ba-hexaferrite stretching band is shifted from wave numbers 573 and 427 cm^{-1} in ferrite to wave numbers 566 and 418 cm^{-1} in the nanocomposite (Fig. 2c), resulting from the formed interaction between Ba-hexaferrite and MWCNTs. The peak at 1636 cm^{-1} in all the spectra is assigned to the water in KBr used for making the pellet sample for FTIR analysis. The peak at 1580 cm^{-1} is also attributed to the C=C stretching mode corresponding to the