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Characterization of magnetic and microwave absorption properties of multi-walled carbon nanotubes/Mn-Cu-Zr substituted strontium hexaferrite nanocomposites

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ABSTRACT

The nanocomposites of multi-walled carbon nanotubes (MWCNT)/$SrMn_xCu_xZr_{2x}Fe_{12-4x}O_{19}$ (x = 0.0, 0.2, 0.3, 0.4 and 0.5) were fabricated. The X-ray diffraction patterns (XRD) confirmed the formation of M-type hexaferrites crystal structure. Fourier transform infrared (FTIR) spectroscopy has been used to consider the chemical bonds in the nanocomposites. From field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), the fabrication of the nanocomposites has been confirmed. The vibrating sample magnetometer (VSM) was used to investigate magnetic properties of the nanocomposites. Microwave absorption properties have been investigated by the vector network analyzer. It is found that the nanocomposites with $x \geq 0.3$ and 7% weight percentage of MWCNT possess the wide bandwidth of 6 GHz. The nanocomposite with the chemical composition of $SrMn_{0.4}Cu_{0.4}Zr_{0.8}Fe_{10.4}O_{19}$-MWCNT has the highest reflection loss, and as a result, it is the most appropriate material among these samples to be used as an electromagnetic wave absorber.

1. Introduction

With recent advances in the microwave technology and high frequency electronics, the research interests in the materials that can reduce the electromagnetic interference and backscattering have been increased [1–3]. The excellent properties of strontium hexaferrite with the chemical composition of $SrFe_{12}O_{19}$ (SrM) such as high Curie temperature, low cost and high chemical stability lead many researchers to consider it as an electromagnetic absorbing material [4,5]. However, there are two main methods to increase the efficiency of strontium hexaferrite in order to be used as an electromagnetic wave absorber. First, it is approved that the substitution of iron atoms by some of the other transition elements leads to a decline in the coercive field which may lead to the shift of reflection loss peak to lower and more applicable frequencies [6]. However, negligible dielectric loss has limited the applications of these kinds of the materials. Either only the magnetic or dielectric loss absorber materials may induce a weak electromagnetic wave absorption property due to the imbalance of the electromagnetic match. Therefore, another method to increase the effectiveness and reflection loss of strontium hexaferrite is to create its nanocomposites with dielectric absorber materials. Recently, a variety of carbon-based materials such as single wall carbon nanotubes, multi-walled carbon nanotubes (MWCNTs), graphene, graphite, carbon-fiber and carbon black powders are proposed as dielectric absorber materials [7–9]. Excellent MWCNT properties such as chemical stability, high aspect ratio, interesting electrical properties, low density and dielectric properties cause it to be an appropriate candidate to be used as a dielectric absorber material.

In this study, we have considered the structural, magnetic and microwave absorption properties of Mn-Cu-Zr substituted strontium hexaferrite-MWCNT nanocomposites. The dielectric and magnetic losses should be in balance to have the optimized reflection loss for a material [10–12]. Adding MWCNTs to the materials would change the dielectric loss, and doping of the ferrites could modify the magnetic loss of the compounds [13].

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Here, we want to achieve the optimized reflection loss for transition metal doped SrM-MWCNT nanocomposites by employing the fixed content of 7 wt.% for MWCNTs and changing the dopant concentration of the transition elements. The nanocomposites of $SrMn_xCu_xZr_{2x}Fe_{12-4x}O_{19}$ (x = 0.0, 0.2, 0.3, 0.4 and 0.5)-MWCNT were fabricated with 7 wt.% MWCNT using the hexaferrite nanoparticles synthesized by the coprecipitation method. It is found that the magnetic and microwave absorption properties of the nanocomposites could be improved by the sufficient amount of MWCNT, and the nanocomposite with the chemical composition of $SrMn_{0.4}Cu_{0.4}Zr_{0.8}Fe_{10.4}O_{19}$-MWCNT is the most appropriate candidate to be used as electromagnetic wave absorber with wide bandwidth and low reflectivity at the Ku-band frequency range.

2. Experimental procedure

The coprecipitation method was employed to prepare the nanoparticles. First, the stoichiometric amounts of starting materials with the chemical compositions of $ZrO(NO_3)_2{\cdot}xH_2O$, $MnCl_2{\cdot}4H_2O$, $CuCl_2{\cdot}2H_2O$, $FeCl_3$ and $SrCl_2{\cdot}6H_2O$ were dissolved in deionized water at 70 °C and stirred to yield a clear aqueous solution. Next, sufficient amounts of 1.5 M NaOH solution was added slowly and dropwise to the solution until a pH level of 13 was reached. The resultant suspension was stirred for one hour. Then, the precipitate was washed for several times until a pH level of 7 was achieved. Finally, the precipitate was filtered and dried at 90 °C and then calcined at 900 °C.

In order to produce nanocomposites with 7 wt.% MWCNT content, the surface of the MWCNTs should be modified for two main reasons. First, it is difficult to disperse MWCNTs in various solutions, and second, the low chemical adjustment between the MWCNTs and the ferrite lead to weak interfacial strength. The dispersion of MWCNTs in the ferrite solutions can be improved by attaching functional groups, such as carboxylic acid groups, on the outer surface of MWCNTs. Besides, the electrostatic interactions between the carboxylic groups with negative charges and the positive cations such as Cu^{+2}, Zr^{+4}, Mn^{+2} and Fe^{+3} lead to the formation of substituted ferrites on the outer surface of MWCNTs. Therefore, the MWCNTs were functionalized with the formation of carboxylic groups on the external surfaces of them using HNO_3, ployacrylic acid (PAA) and high power ultrasound in the process. Next, the functionalized MWCNTs were dispersed in the mixture of PAA and distilled water using the sonication operation for 30 min. Then, the nanoparticles of doped-SrM were added to the mixture and sonicated again for 90 min, and finally the solution was dried at 90 °C.

The formation of M-type hexaferrite phase was examined by X-ray diffraction (XRD) spectroscopy with Cu-Kα radiation. The nature of chemical bonds was investigated using Fourier transform infrared (FTIR) spectroscopy. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were employed to investigate the surface morphology of the prepared samples. The magnetic properties of the nanocomposites were investigated using vibrating sample magnetometer (VSM). Microwave absorption properties of the samples were also assessed by vector network analyzer.

Table 1
The lattice constants *a* and *c*, and the crystallite size *D* of the prepared samples.

x	a (Å)	c (Å)	D (nm)
0.0	5.85	22.91	41.77
0.2	5.86	23.02	41.76
0.3	5.87	23.07	41.75
0.4	5.87	23.09	41.75
0.5	5.88	23.11	41.74

3. Results and discussion

3.1. Structural properties

The XRD patterns of the Mn-Cu-Zr substituted SrM-MWCNT nanocomposites are represented in Fig. 1. The same pattern for the undoped strontium hexaferrite nanoparticles is also given for comparison. We find that the diffraction peaks at $2\theta = 30.32^o$, 32.35^o, 34.18^o, 37.12^o, 40.38^o and 42.53^o are attributed to the (110), (107), (114), (203), (205) and (206) planes of M-type structure of magnetoplumbite ferrite. The diffraction peak at about 26.40^o in the XRD pattern of the nanocomposites is due to MWCNTs that can be indexed to the (002) reflection of CNTs [10,13]. The hexagonal lattice parameters (*a* and *c*) could be calculated from the XRD patterns of the samples [1]. The results of our calculations are listed in Table 1. As we can see from this table, the lattice parameter *a* remains almost constant, while *c* is

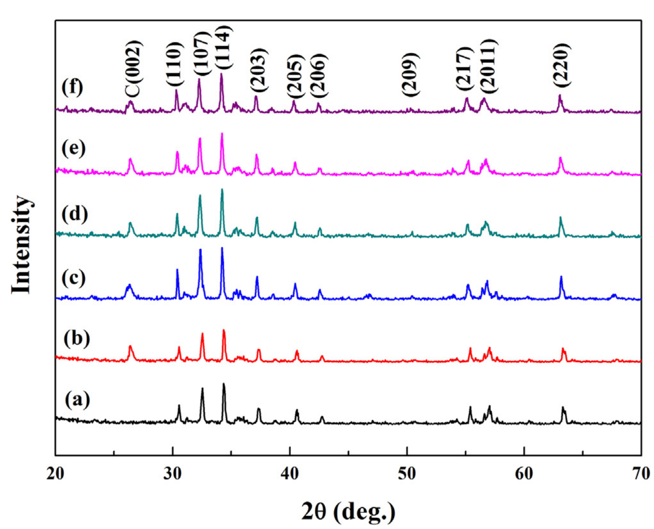

Fig. 1. The XRD patterns of (a) undoped strontium hexaferrite, and $SrMn_xCu_xZr_{2x}Fe_{12-4x}O_{19}$-MWCNT nanocomposites for (b) x = 0.0, (c) x = 0.2, (d) x = 0.3, (e) x = 0.4, and (f) x = 0.5.

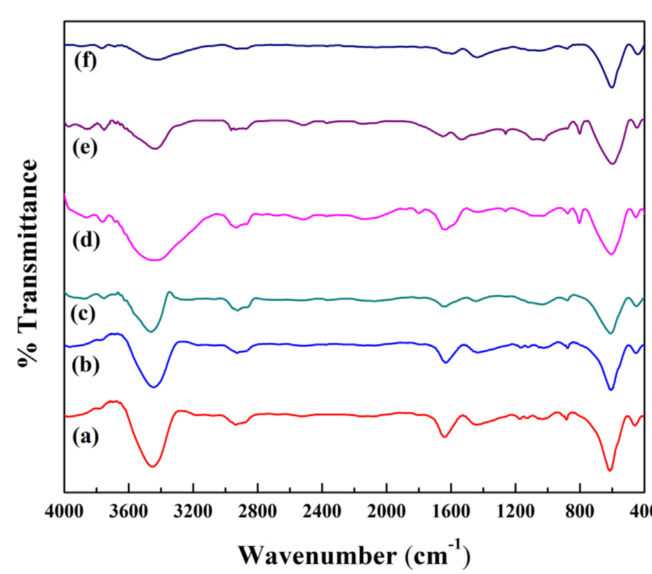

Fig. 2. FTIR spectra of $SrMn_xCu_xZr_{2x}Fe_{12-4x}O_{19}$-MWCNT nanocomposites for (a) x = 0.0, (b) x = 0.2, (c) x = 0.3, (d) x = 0.4, (e) x = 0.5, and (f) the nanoparticles of $SrMn_{0.5}Cu_{0.5}ZrFe_{10}O_{19}$.