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$Ba_{0.69}Sr_{0.17}Cd_{0.07}Zn_{0.07}Fe_{12}O_{19}$ nanostrucutres/conducting polyaniline nanocomposites; synthesis, characterization and microwave absorption performance

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ABSTRACT

In this study, conductive and magnetic polyaniline (PANi) nanocomposites containing nanoparticles and nanorods with a special stoichiometry of $Ba_{0.69}Sr_{0.17}Cd_{0.07}Zn_{0.07}Fe_{12}O_{19}$ were prepared by in situ polymerization. Two different reflux and solvothermal procedures followed by heating treatments were adopted to synthesize the magnetic cores. The particle and rod morphologies in nanoscale were obtained from these methods, respectively. Ethylenediaminetetraacetic acid (EDTA) and ethylenediamine (en) were employed as the soft templates and complexing agents. The magnetic properties of the prepared samples were characterized on a vibrant sample magnetometer (VSM) with maximum saturation magnetization values of 66.59, 65.09, 46.80 and 17.07 emu/g for nanoparticles, nanorods, nanoparticle/PANi and nanorod/PANi composites, respectively. The structure of the M-type hexagonal ferrite for magnetic cores was evidenced by X-ray diffraction patterns (XRD). Meanwhile, the absorption capability of electromagnetic waves related to these composites was evaluated in the X-band (8–12 GHz). As a result of this operation, these products showed the maximum reflection loss of −16 dB.

1. Introduction

In recent years, the design and fabrication of electromagnetic waves absorbers has attracted an increasingly attention to suppress the electromagnetic interference (EMI) stimulated by the wide applications of electronic devices. The magnetic materials, especially ferrites, are an important class of electromagnetic waves absorbers at the range of gigahertz (GHz) frequency [1–6]. Different kinds of ferrites are employed in the air-space technology and military domains such as dielectric and magnetic filler materials in the electromagnetic wave shielding and protective agents of security devices [7–10]. M-type hexagonal ferrites are a suitable choice for microwave absorbing operation due to their strong magnetic losses at the range of GHz frequency. These materials have the magnetoplumbite structure with the formula of $M–Fe_{12}O_{19}$ or $MO·6Fe_2O_3$. The large crystal anisotropy, high electrical resistivity and proper stability are the considerable characteristics of this structure [11–13]. Many methods are used to prepare magnetic ferrites such as hydrothermal [14], mechanochemical reaction [15], sol–gel method [16], precipitation route [17], citrate precursor method [18] and reflux procedure [19]. The synthesis of these nanomaterials using reflux process was demonstrated in our earlier work [20]. The reflux and also hydrothermal/solvothermal reactions are the facile procedures with high efficiency which can be used for preparation of the magnetic nanostructures in large quantities. Although the pure magnetic ferrite nanoparticles have an excellent performance for microwave absorbing, the use of ferrites alone cannot fulfil the desired purposes. The product weight, synthesis costs and application potential of these materials in various devices are the essential subjects in the field of microwave absorption. Therefore, many investigations were carried out to combine these materials with the appropriate compounds [19,21]. Conductive polymers [e.g., polyaniline (PANi)] are not only suitable candidates for incorporation with the ferrite but also are well known absorbents of electromagnetic waves [22]. This polymer is a unique conductive material with the simple and economical synthesis, thermal and chemical stability, and low specific mass. Therefore, PANi can be an appropriate choice for obtaining various purposes [23,24]. Currently, there have been many reports on the synthesis of composites including magnetic oxides and PANi with different nanostructures. To the best of our knowledge, however, investigations on the prepared ferrite nanocomposites have not yet been reported [25].

In this study, we report an extension in the chemical free-surfactant methods to synthesize the PANi nanocomposites with the magnetic core of $Ba_{0.69}Sr_{0.17}Cd_{0.07}Zn_{0.07}Fe_{12}O_{19}$. Calcination planning was used to achieve the single phase of M-type hexagonal

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ferrite. The conductive, magnetic and microwave absorption properties of the particle and rod shaped ferrite/PANi nanocomposites have been investigated in detail. The structural and morphological characterizations were performed using FT-IR, XRD, SEM, VSM and EDX techniques.

2. Experimental procedures

2.1. Materials of synthesis

The pure synthesis grade of iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), strontium nitrate ($Sr(NO_3)_2$), barium chloride ($BaCl_2.2H_2O$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2$. $4H_2O$), zinc chloride ($ZnCl_2$), ethylenediaminetetraacetic acid (EDTA), ethylenediamine (en, C_2H_4 $(NH_2)_2$) and aniline monomer were supplied as initial reagents to synthesize purposed nanostructures. All of the chemicals used in this work were purchased from Merck Co. and used without further purification.

2.2. Synthesis of magnetic nanoparticles (S1)

Magnetic nanoparticles of the hexagonal ferrite with formula $Ba_{0.69}Sr_{0.17}Cd_{0.07}Zn_{0.07}Fe_{12}O_{19}$ (S1) were synthesized by reflux reaction similar to the process reported in our earlier work [20]. Briefly speaking, 1.1 g of the ethylenediaminetetraacetic acid (EDTA) as a complexing agent was dissolved in 30 mL deionized water. As starting materials, stoichiometric weights of $FeSO_4.7H_2O$ (19.40 g, 69.8 mmol), $BaCl_2.2H_2O$ (0.97 g, 4 mmol), $Sr(NO_3)_2$ (0.21 g, 1 mmol), $Cd(NO_3)_2.4H_2O$ (0.0.9 g, 0.4 mmol) and $ZnCl_2$ (0.05 g, 0.4 mmol) were dissolved in sufficient amount of deionized water and poured into the reflux flask. The solution was allowed to stir for 1.5 h at 90 °C. Subsequently, 20 mL ammonia solution (5 M) was slowly dropped into the mixture of reflux and the reaction continued at the same temperature for 3 h. the reaction was entirely performed under nitrogen atmosphere in order to prevent further oxidation of the prepared nanoparticles and conversion of them to another phase of ferrite. After completing reaction, the resulting precipitation was collected, washed and dried at 70 °C for 12 h. Following this step, the obtained precursor was heated in two stages: first, 450 °C for 2 h and second, 850 °C for 2 h with rate of 10 °C/h under nitrogen atmosphere to reach the desired structure. In addition, a parallel reaction with the above procedure was carried out using EDTA solution of 0.5 M (S2) to study the effect of EDTA concentration on the morphology of mentioned ferrite.

2.3. Synthesis of magnetic nanorods (S3)

The nanorod structure (S3) with the same stoichiometry of (S1) was prepared using the solvothermal reaction. The stoichiometric weights of $FeSO_4.7H_2O$ (19.40 g, 69.8 mmol), $BaCl_2.2H_2O$ (0.97 g, 4 mmol), $Sr(NO_3)_2$ (0.21 g, 1 mmol), $Cd(NO_3)_2.4H_2O$ (0.0.9 g, 0.4 mmol), and $ZnCl_2$ (0.05 g, 0.4 mmol) have been used as the starting materials. These reagents were dissolved in a mixture of deionized water and ethylendiamine (en) with the volumetric ratio of 1:2 under continual stirring for 1.5 h at ambient conditions. The prepared solution was transferred into a 230 mL Teflon-lined stainless autoclave and put in the oven for 48 h at 120 °C. Then, the obtained precursor was filtered and washed several times with distilled water to remove the excess ions e.g. $(SO_4)^{2-}$, Cl^-, $(NO_3)^-$ and unreacted reagents. At the end, products were dried at 70 °C for 12 h. Meanwhile, another sample (S4) was synthesized in accordance with the mentioned process for S3 using doubled amount of ethylenediamine.

2.4. Preparation of PANi/particle shaped and rod shaped ferrites nanocomposite (S5, S6)

With reference to more uniform morphology of the obtained samples, S1 and S3, these samples were selected as filler materials for polymerization step and further characterization.

PANi/particle shaped ferrite nanocomposite was prepared by chemical oxidative polymerization according to the following recipe: 0.2 g of aniline monomer was injected to the 200 mL of 0.1 M HCl solution with continual stirring for 15 min. Then, 0.1 g of synthesized nanostructure (S1), previously dispersed in an appropriate amount of distilled water using ultrasonic treatment for 30 min, was added into the solution containing monomer. Then, this suspension was resonicated for 1 h. The prepared mixture was mechanically stirred in ice-water bath (5 °C). Concurrently, an aqueous solution (20 mL) of ammonium per sulfate (APS, 0.63 g dissolved in 50 mL distilled water) as an oxidizing agent was gently added to the above mixture. This process continued for 8 h to complete polymerization reaction. The dark green precipitate (S5) was filtered and washed several times with distilled water and then dried at 70 °C for 24 h. Preparation of PANi/rod shaped ferrite nanocomposite (S6) is similar to the described recipe for S5 except using the specimen of (S3) as filler.

2.5. Characterization

The powder X-ray diffraction (XRD) measurements were carried out by a Jeoljdx-8030 diffractometer with monochromatized CuKα radiation (λ = 1.5418 Å, 40.0 kV, 30.0 mA). Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu-8400S spectrometer in the range of 400–4000 cm^{-1} using KBr pellets. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy analysis (EDX) were taken on a Philips (XL-30) with gold coating. The magnetic properties (intrinsic coercivity, saturation, The *M–H* hysteresis loops and remanent magnetization) were recorded by using a vibrating sample magnetometer (VSM, MDK6) which has been made by the efforts of the Magnetis Daghigh Kavir Company in Iran. The EMI shielding properties were evaluated using a vector network analyzer system (Agilent ENA 20 GHz). Variation of reflection loss in (dB) with respect to frequency in the range of 8–12 GHz was studied.

3. Results and discussion

3.1. X-ray diffraction patterns and EDX analyses

Fig. 1 displays the XRD patterns of sample (S1) calcined at different heating treatments. The marked peaks in all patterns indicate that the hexagonal M-type phase is the major component in all prepared samples. The XRD pattern shown in Fig. 1a is related to the sample before calcination. This pattern indicates the presence of hexagonal M-type ferrite phase with identified peaks according to the JCPDS cards Nos. 84-0757 and 33-1340. Moreover, the secondary peaks recognized in this pattern can be attributed to cubic γ-Fe_2O_3 (JCPDS card No. 039-0238) phase and also the partial hexagonal phase of $BaFe_2O_4$ (JCPDS card No. 026-0158). Hence, identification of the hexagonal structure as a single phase is difficult. Heat-treatment was used to improve the crystalline structure of the prepared ferrites. By heating the sample from ambient temperature to 450 °C for 2 h, diffraction major peaks were matched with characteristic peaks of hexagonal ferrite shown in Fig. 1b. Although this pattern is compatible with the JCPDS cards Nos. 078-0131 and 72-0739, there are still partial diffraction signals of

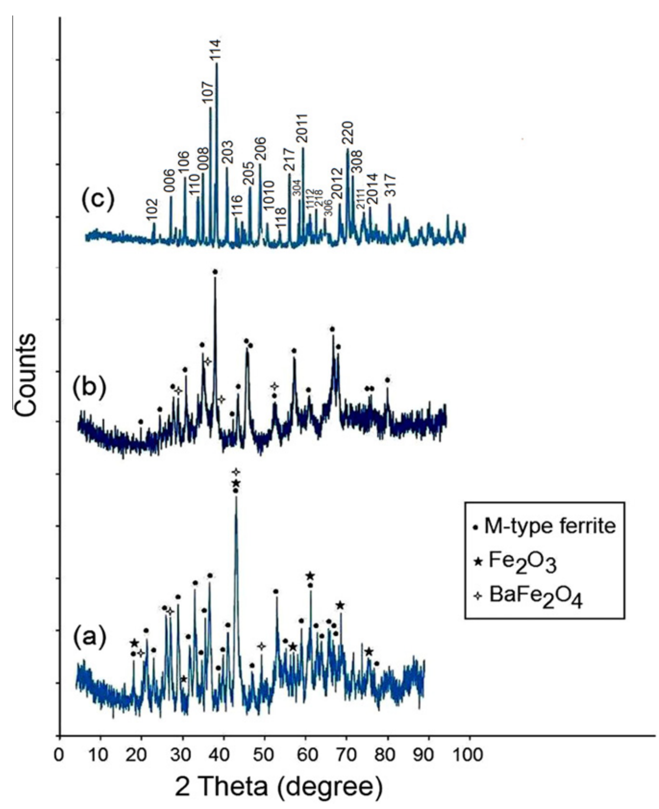

Fig. 1. X-ray diffraction patterns of sample S1 before calcination (a), calcined at 450 °C for 2 h (b) and calcined at 850 °C for 2 h (c).