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Structural, magnetic and dielectric properties of (PANI)–$Ni_{0.5}Zn_{0.5}Fe_{1.5}Cr_{0.5}O_4$ nanocomposite

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ABSTRACT

Polyaniline (PANI)-$Ni_{0.5}Zn_{0.5}Fe_{1.5}Cr_{0.5}O_4$ (NZFCO) nanocomposites are conducting polymer–ferrite, which belongs to magneto-polymeric materials. They have very useful electromagnetic properties with new functions. The nanocomposites were synthesized in situ by polymerization of PANI in the presence of NZFCO nanoparticles. The results of XRD, FTIR spectra and TEM showed the presence of the two intended phases. The crystallite sizes measured were found to be in the nanorange (5–11 nm) which are almost in agreement with XRD data. The selected area electron diffraction (SAED) pattern of the nanocomposite, showed the superposition of both PANI ring and the single spot of the ferrite nano-crystallite {1 1 1} reflections, which confirms that PANI is covering the ferrite nanocrystallites. The DTA analysis indicated the high temperature stability of the nano-composite phase (347 °C) compared with PANI (270 °C). The highest magnetic saturation (M_s) was found for the nano-composite sample which have PANI concentration of (40% and 60%). The crystallite sizes, strains and change in lattice parameters were found to increase by increasing the percentage of PANI. The ac conductivity, dielectric constant and dielectric loss of all sample composition are much higher than that of PANI, the highest is for the sample which has has (60%) PANI concentration. The loss tangent were found to have very high values in the microwave range for certain concentrations and to have very low values for some other concentration with no definite systematic correlation. The temperature dependence of dielectric constant revealed a diffused phase transition (DPT) at higher temperature with higher dielectric constant of many order of magnitudes. The properties of magneto-polymeric nanocomposite are greatly influenced by the percentage of its component phases and the degree of mixing between the two phases. In general the different variety of the results obtained by just changing the relative percentage of PANI–NZFCO, made the present studied samples to be useful in many technological applications.

1. Introduction

Composite made of more than one material can integrate their properties component in one single material. Materials composed of conducting polymers and magnetic materials can provide novel or enhanced properties for various applications. These materials are called magnetopolymeric materials. Conducting polymer–ferrite composites with an organized structure provide a new functional hybrid between organic and inorganic materials [1]. The properties of magnetopolymeric nanocomposite are greatly influenced by the size scale of its component phases and the degree of mixing between the two phases [2,3]. These characterisations are very important for defining their properties, such as electrical conductivity [4], magnetic behavior [5], catalytic effects [6], microwave absorption [7], capacity for drug delivery and controllable release [8], and use in optoelectronics and microcavity resonance [9].

Moreover these nanocomposites should have good dielectric and magnetic loss in order to improve their capacities for microwave absorption or electromagnetic shielding. It is known that the conducting polymers can effectively shield electromagnetic waves generated from an electric source, whereas, electromagnetic waves from a magnetic source, especially at low frequencies, can be effectively shielded only by magnetic materials. Thus, fabrication of the conducting PANI–magnetic ferrite composites can be used successfully as electro magnetic interference shielding (EMI), good shielding effectiveness can be achieved for various electro-magnetic sources. Different nanocomposites formed of PANI and ferrite have been recently synthesized [10,11], each of these composites showed very interesting electromagnetic properties. The magnetic ferrite used in this work is $Ni_{0.5}Zn_{0.5}Fe_{1.5}Cr_{0.5}O_4$ which is a mixed ferrite whose chemical formula $(M^{2+}_{1-\lambda}Fe^{3+}_{\lambda})[M^{2+}_{\lambda}Fe^{3+}_{2-\lambda}]O_4$ where parentheses and square brackets represent the tetrahedral site (A) and Octahedral site (B) respectively [12], λ represent the fraction of A site (degree of inversion) occupied by Fe^{3+} cations. NZFCO has a giant dielectric constant in the frequency range of 10^6 and a

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dispersive phase transition at around 305 K [13]. The aim of the present work is to use the sol–gel technique and in situ polymerization methods to prepare (PANI) – NZFCO nanocomposites, in order to; study; the microstructures, electric and magnetic properties of the prepared composites. These information are very important in characterizing the suitability and the stability of these materials and its different function in different applications.

2. Sample preparation and analysis

2.1. Samples preparation

NZFCO nanoparticle was prepared by the sol–gel method, using nitrates of iron, nickel, chromium, zinc, citric acid and deionised water as a solvent. The stoichiometric ratio between metals and citric acid was 1.05. The gel was obtained by stirring all the ingredients at room temperature for about 1 day, followed by drying at 200 °C for 2 h then drying at 400 °C for 1 h and cooling to room temperature. We have to take into our consideration not to increase the sintering temperature above 400 °C, since it was found that above this temperature, another second phase of Fe_2O_3 start to appear. PANI was prepared using homogeneous aqueous solution of monomer and oxidant in the following ratio and steps: Anilinium chloride (ANCl, 20 mmol) was dissolved in 50 ml distilled water in a volumetric flask. Ammonium persulfate (APS, 25 ml mol) was dissolved also in 50 ml distilled water. The addition of oxidant solution was completed in 30 min, after that, stirring was continued for 24 h. After 24 h, green precipitate was collected and washed with HCl of 1 M, distilled water and ethanol. Finally, the sample was dried at 70 °C in vacuum oven.

PANI–NZFCO nanocomposites were prepared by a simple in situ polymerization method of PANI in the presence of different percentage of NZFCO nanoparticles. (20, 40, 60, and 80 wt%) with respect to the aniline monomers which were dispersed in ANCl solution (nanomaterial/ANCl, weight ratio), then after that, to follow the remaining steps used in pure polymer preparation, previously mentioned before.

2.2. Samples analysis

Phases identification for the prepared nanocomposites were confirmed by X-ray diffraction using Philips diffractometer (X'pert MPD) with Cu Kα radiation. The crystal structure and microstructure were refined by using Rietveld method, applying MAUD program [14]. Simultaneous refinement of; structural parameters (lattice parameters, atomic coordinates, displacement parameters) and microstructures (crystallite sizes (D), and r.m.s. lattice microstrains) were identified with good accuracies. The U, V, W parameters of instrumental broadening, instrumental asymmetry and the profile shape of the reflections were estimated for the present setting of the diffractometer, using a LaB6 standard sample. These instrumental parameters were kept fixed during the subsequent structural and microstructural refinements of the different parameters. Due to the anisotropy in the profiles shape of the diffraction lines, discrepancies in measuring the different obtained parameters were introduced. Accordingly the Popa anisotropic model [15] has been used. The process of successive profile refinements modulates the different structural and microstructural parameters of the simulated pattern to fit the experimental diffraction pattern. No absorption correction was taken into consideration and the scattering background was refined with a 5th order polynomial. The morphological shape and electron diffraction of the fine particles were investigated by the high resolution transmission electron microscope (HRTEM). The infrared measurements were performed in the transmission mode, using a Fourier Transform Infra Red (FTIR) Biorad spectrometer FTS-40A with dynamic alignment and a spectral resolution of 2 cm^{-1} in the range 400–4000 cm^{-1}. 0.2 mg sample per 200 mg KBr was pressed into pellets. Thermal gravimetric analysis (TG/DTA) was carried out through SDT Q600 V8.3 Build 101 at a heating rate of 20 °C/min in inert (N_2) gas atmosphere and in the temperature range from room temperature to 900 °C. The magnetic properties of the composite samples were measured by using vibrating sample magnetometer (VSM; 9600-1 LDJ, USA) at room temperature. The pure PANI, the pure ferrite and the resulted nanocomposite powder were pressed into a pellet form of 10 mm in diameter and 1–2 mm in thickness. The pellet was covered by silver paste on both sides to act as electrode of ohmic contact for the dielectric measurements, thin copper wires acted as leads. Dielectric and impedance spectroscopy measurements were carried out using LCRHI-Tester (HIOKI3532-50) in the frequency range 42 Hz–5 MHz at different temperatures. The dielectric constant was calculated by using the following relation: $\varepsilon = \varepsilon' - j\varepsilon''$, the first term is the real part of dielectric constant ε' which describes the stored energy while the second term ε'' is the imaginary part of dielectric constant, which describes the dissipated energy. The real dielectric constant is measured experimentally from the relation; $\varepsilon' = \frac{C_p d}{\varepsilon_0 A}$, where C is the measured value of the capacitance of a the sample in F, d is the thickness in m, A is the surface area in m^2 and ε_0 the dielectric permittivity of air. The imaginary part of the dielectric constant was calculated using the following relation $\varepsilon'' = \varepsilon' \tan\delta$ where $\tan\delta$ is the dielectric loss. From the dielectric constant and dielectric loss, the ac conductivity (σ_{ac}) of the samples was calculated using the following relation: $\sigma_{ac} = \omega\varepsilon'\varepsilon_0 \tan\delta$, where ω is the angular frequency.

3. Results and discussion

3.1. X-ray diffraction and morphological analysis

Fig. 1(i) a–f shows XRD patterns of pure PANI and PANI–$Ni_{0.5}Zn_{0.5}Fe_{1.5}Cr_{0.5}O_4$ nanocomposites having percentage of PANI (100%, 80%, 60%, 40%, 20% and pure ferrite (NZFCO), respectively. The XRD pattern showed mixture of both mixed materials; pure phase of PANI and pure phase of ferrite, without the presence of any foreign phases. The NZFCO shows single phase spinel structure with no extra reflections, moreover, the diffraction pattern lines indexed fit the corresponding diffraction pattern of the spinel ferrite structure. The Rietveld refinement using MAUD program [14] of NZFCO and 40% PANI–60% NZFCO samples is shown in Fig. 1(ii and iii), from the refinement the lattice parameters, the crystallite sizes and the strains in each sample were calculated. The crystallite size of the ferrite were found to be in the range 5–11 nm, Table 1 shows the crystallite sizes and the average strain of the ferrites phase. The typical XRD pattern of PANI (Fig. 1(i)a) shows several broad diffraction peaks in the region of (15–31°) which indicates its semi-crystalline nature. The intensity of the characteristic diffraction peaks of PANI in the nanocomposites are weakened with increasing NZFCO content and they are almost disappearing and broaden in the nanocomposites sample which has (20% PANI and 80% NZFCO). This disappearance indicates that the concentration of 20% PANI is completely absorbed on the surface of 80% NZFCO ferrite. This may indicates also that the force of adhesion between the interfaces of PANI and NZFCO at this percentage are very strong. Fig. 2 shows that the smallest crystallite size and strains are seen for the pure $Ni_{0.5}Zn_{0.5}Fe_{1.5}Cr_{0.5}O_4$ (100%) and the largest crystallite size and strains are due to the nanocomposites (80% PANI–20% NZFCO). The crystallite sizes are increased by increasing the percentage of PANI, this is obvious because by increasing the percentage of PANI in the sample it will increase the thickness of the deposited layer