



Preparation of magnetic and conductive Ni–Gd ferrite-polyaniline composite

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Abstract

In this work, particles of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ were coated with polyaniline (PANI) during the *in situ* polymerization of aniline in aqueous solution. Different ferrite/aniline ratios were selected in order to study magnetic and conductivity properties with increasing fraction of PANI. In a previous work, the addition of Gd in the structure of nickel ferrites obtained from mixed Gd, Fe and Ni citrates has been investigated in order to explore the possibility of Gd for Fe substitution in the solids. The ferrite-PANI composites were characterized by X-ray diffraction (XRD) and infrared (IR) spectroscopy. The changes on the magnetic and conductive properties after polyaniline coating were investigated. The coercivity is almost unchanged, while the saturation magnetization drastically decreases. It was found that the conductivity at room temperature increases from 4×10^{-3} to 9.6×10^{-3} S/cm when ferrite content changed from none to 24.5 wt/wt%. The conductivity of all measured samples decreased with decreasing temperature, exhibiting typical semiconductor behavior.

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Conducting polymers have attracted considerable attention for their potential applications in various fields such as electromagnetic interference (EMI) shielding, rechargeable batteries, electrodes and sensors, corrosion protection coatings and microwave absorption [1–4]. Conducting polymer-inorganic composites possess not only the nature of the flexibilities and processibility of polymers but also the mechanical strength and hardness of inorganic compounds.

Nickel-ferrites are found to be the most versatile technological materials specially suited to high-frequency applications on account of their high resistivity [5]. The electromagnetic properties of the Ni-ferrites may be modified by the doping with rare earth (R) cations [6]. In a previous work, [7] we have investigated the structure of various Gd-doped ferrites ($\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$). The electromagnetic measurements indicate an enhancement of the magnetic permeability for $x = 0.05$ [8], being x the atomic fraction of Gd in the formula unit. Materials comprising a

ferromagnetic component and a conducting polymer have recently been investigated in several studies that concentrated on the preparation of nano-colloidal iron oxides, $\gamma\text{-Fe}_2\text{O}_3$ [9,10] and Fe_3O_4 [11–14], and their subsequent modification with conducting polymers, specifically polyaniline (PANI) or polypyrrole. Most of the papers have reported the magnetic and electrical properties of the resulting nano-sized composite materials. Less attention has been paid to the coating of larger micrometer-sized magnetic particles. Several studies only concerned the surface modification of ferrites with conducting polymers. Manganese–zinc ferrite particles of micrometer size have recently been coated with PANI by using a chemical oxidation of aniline [15]. It was observed that the magnetic properties of a ferrite were influenced by a coating of a conducting polymer. Stejskal et al. [16] reported that even a low amount of PANI, 1.8 wt%, produced on the zinc ferrite particles results in a high degree of coating, 45% [16].

In this paper, magnetic and conducting composites containing polyaniline-coated $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ ferrite were synthesized by *in situ* polymerization of aniline on

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the surface of ferrite particles. The samples were characterized by various experimental techniques, and magnetic and electrical properties were investigated.

1. Experimental

Samples of nominal composition $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ were prepared according to [8] from Fe (III), Gd (III) and Ni (II) citrates. The obtained solids were sintered at 1100°C for 2 h.

Ferrite-PANI composites of various compositions (C1: 10.7%, C2: 24.5% and C3: 32.3%) were prepared by the *in situ* polymerization of aniline in aqueous solution of hydrochloric acid, with different amount of ferrite powder. In a typical procedure, 0.15 g of ferrite was suspended in 10 ml of 1 M HCl solution and stirred in ultrasonic bath for 1 h to get a homogeneous dispersion (A). Separately, a chloridric solution of aniline 1.2 M, was prepared (B). The mixture (A+B) was stirred while an ammonium peroxydisulfate 0.9 M solution was slowly added to the suspension, at 0°C , with constant stirring. Finally, a 6 M NH_3 solution to $\text{pH} = 10$, was added. The composite ferrite-PANI was obtained by filtering and washing the suspension with distilled water, methanol and acetone. Samples were dried at 60°C in a vacuum oven. For electrical measurements, ferrites coated with PANI were immersed in aqueous solution of chloridric acid to protonate PANI coating.

The content of PANI in the coated ferrites was determined as an ash. Diffraction patterns were recorded in a Siemens D5000 diffractometer using $\text{Cu K}\alpha$ radiation. The relative crystalline size was determined from the full-width at half-maximum (FWHM) of the 311 X-ray diffraction (XRD) peak by employing Debye Scherrer's formula.

Infrared (IR) spectra were recorded using a fully computerized Thermo Nicolet NEXUS 870 FTIR spectrometer (Nicolet USA). Magnetic measurements of the composite powders were performed at room temperature using a vibrating sample magnetometer (VSM), Lakeshore equipment, with an external field of up to 1.5 T. The electrical conductivity of pellets was measured at room temperature using the capacitor method with silver paint. Electrical resistivity of pellets was measured using a physical property measurement system made by quantum design (PPMS) in a large temperature range (10–300 K).

2. Results and discussion

Fig. 1 shows XRD patterns of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ nanoparticles (P) and PANI– $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ composites with different ferrite:PANI ratio wt/wt%. (C1–C3). $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ nanoparticles (P) show the characteristic peaks at $2\theta = 30.55^\circ, 35.94^\circ, 37.58^\circ, 43.64^\circ, 54.07^\circ, 57.63^\circ, 63.26^\circ, 71.76^\circ$ with the reflection of Fd3m cubic spinel group, which indicates the formation of a single-spinel phase. Crystalline size from XRD pattern is near 50 nm.

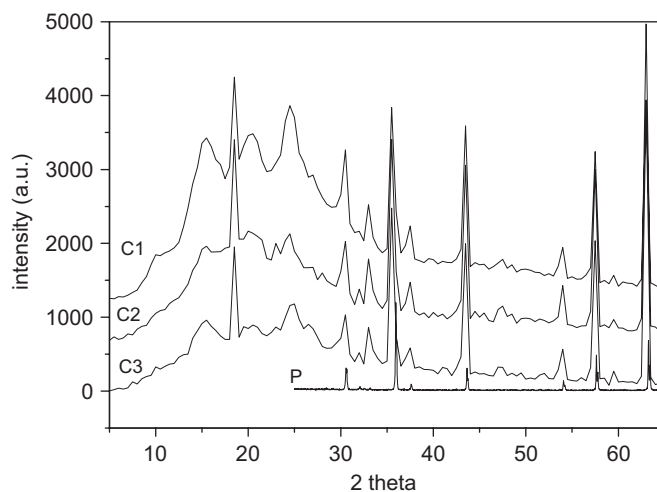


Fig. 1. XRD patterns of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ nanoparticles (P) and of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites with different ferrite: PANI ratio (%wt/wt) (C1: 10.7%, C2: 24.5% and C3: 32.3%).

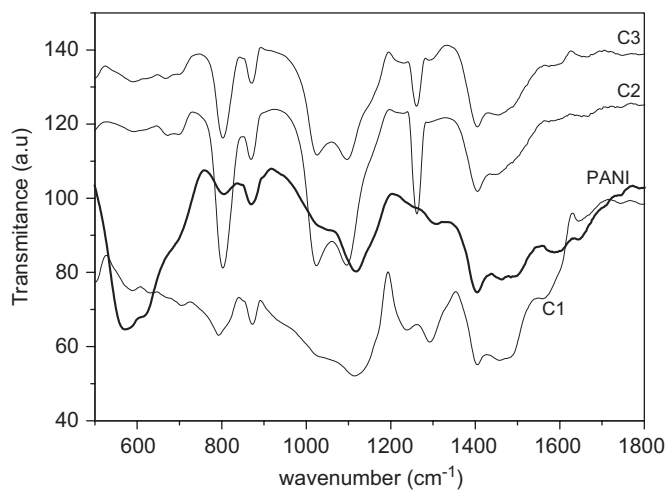


Fig. 2. FTIR spectra of PANI and of the $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites (C1, C2 and C3).

The XRD of the composite samples (C1–C3) exhibit both the characteristic peaks of the $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ ferrite and the broad diffraction peaks of PANI at the angles $2\theta = 15.2^\circ, 20.4^\circ$ and 24.5° , indicating that PANI has some degree of crystallinity. The relative intensity of these peaks might differ, depending on the conditions of the polymerization process.

Fig. 2 shows the Fourier transform infrared (FTIR) spectra of PANI and of the $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites (C1–C3). The part of the spectrum $<2000\text{cm}^{-1}$ shows some notable differences for PANI powders dispersed in KBr pellets.

These are observed especially in the positions of the main peaks at 1583 and 1456cm^{-1} corresponding to quinone ($\text{N}=\text{Q}=\text{N}$) and benzene stretching ring-deformation ($\text{N}-\text{B}-\text{N}$). These modes in the PANI sample show a red shift in the $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites. In the

spectrum of PANI base, the 1309 cm^{-1} band is assigned to the C–N stretch of secondary aromatic amine and 800 cm^{-1} band to an aromatic C–H out-of-plane bending vibration [17]. These bands are slightly moved in the composite samples. These results indicate that, probably, there is some interaction between $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ particles and PANI backbone.

Fig. 3 shows the hysteresis loops obtained for the three composites (C1–C3) as well as for the ferrite nanoparticles (P). The values of saturation magnetization M_s are 5.1 emu/g for C1, 8.8 emu/g for C2 and 13.7 emu/g for C3. As expected, the saturation magnetization decreases as the ferrite fraction decreases. The values obtained for the different composites are consistent with the saturation magnetization of the nanoparticles (44.2 emu/g) and the fraction of PANI in each sample. The coercivity is approximately the same in all the samples ($75 \times 10^{-4}\text{ T}$) which indicates that the PANI content is not high enough in any of the composites to prevent the interaction among the particles. In particular, in sample C1—which has the highest PANI content—the distance between two particles of ferrite is $\sim 90\text{ nm}$, a value comparable to the diameter of the ferrite particle (50 nm). So, the ferrite particles cannot be considered isolated even in composite C1. The effect of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ content on the conductivity of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites, at room temperature, was investigated and shown in Fig. 4. It was found that the conductivity increases from 4×10^{-3} to $9.6 \times 10^{-3}\text{ S/cm}$ when the ferrite content changed from none to 24.5 wt\%/wt\% . This is consistent with the results of PANI/ TiO_2 reported by Su et al. [13]. In the disordered system like the conducting polymers, microscopic conductivity depends upon the doping level and conjugation length while the macroscopic conductivity depends on some external factors like compactness of the sample, orientation of the

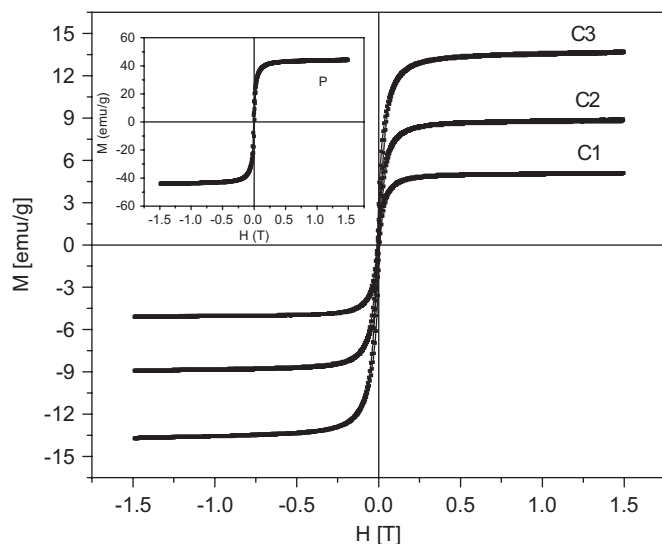


Fig. 3. Magnetization as a function of the applied field of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites with different ferrite: PANI ratio wt/wt%. (C1: 10.7%, C2: 24.5% and C3: 32.3%). The inset shows the curve obtained for $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ nanoparticles (P).

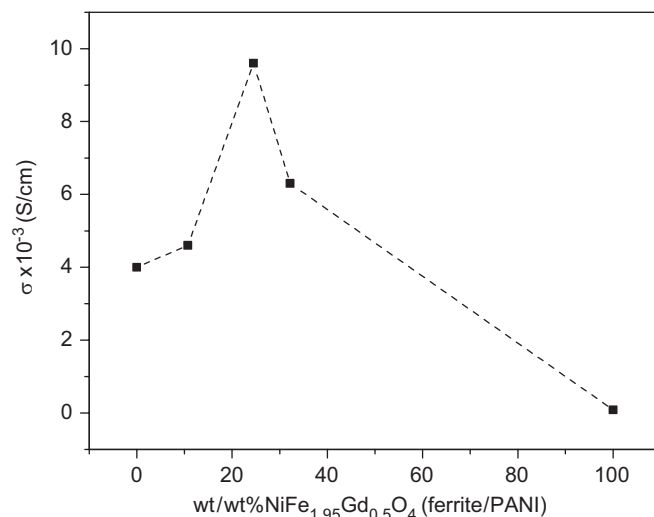


Fig. 4. Effect of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ content in the composites on the conductivity of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI nanostructures at room temperature.

microparticles, etc. [14]. For the $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites, on the one hand, the intrinsic microscopic conductivities are more or less equal, because of the PANI being polymerized in identical conditions. On the other hand, as the PANI content in the composites lowered, the change in compactness became more significant. As a result, the weak links between grains are increasingly improved and the coupling through the grain boundaries becomes stronger leading to the improvement in macroscopic conductivity measured in the pellets. For higher ferrite contents the conductivity decreases. This tendency of decreasing the conductivity after ferrite particles introduction is quite typical [15–19] and may be due to partial blockage of the conductivity path by the ferrite nanoparticles dispersed in the PANI matrix.

The temperature dependence of conductivity of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites with different ferrite contents was measured between 10 and 300 K (Fig. 5). The conductivity of all the measured samples decreased with decreasing temperature, exhibiting typical semiconductor behavior. The data are best fit to the relationship of $\ln \sigma$ vs. $T^{-1/2}$ (graph not shown). These plots exhibit a good linear dependence having a linearity factor of 0.9858, 0.9990, 0.9902 and 0.9986 for C1–C3 and PANI, respectively. So, it is reasonable to believe that the temperature dependence of conductivity of all these ferrite-PANI nanostructures is in agreement with the one-dimensional variable range hopping (1D-VRF) model proposed by Mott [20], which proposes: $\sigma(T) = \sigma_0 \exp(-(T_0/T)^{-1/2})$, where $T_0 = 8 \alpha / Z k_B N(E_F)$ is the hopping barrier, α^{-1} is the location length, $N(E_F)$ is the density of states at the Fermi level, k_B is the Boltzmann constant, and Z is the number of nearest neighbor chains.

Thus, plotting $\ln \sigma$ vs. $T^{-1/2}$ one can obtain the T_0 value corresponding to the effective energy separation between localized states which is a measure of the degree of

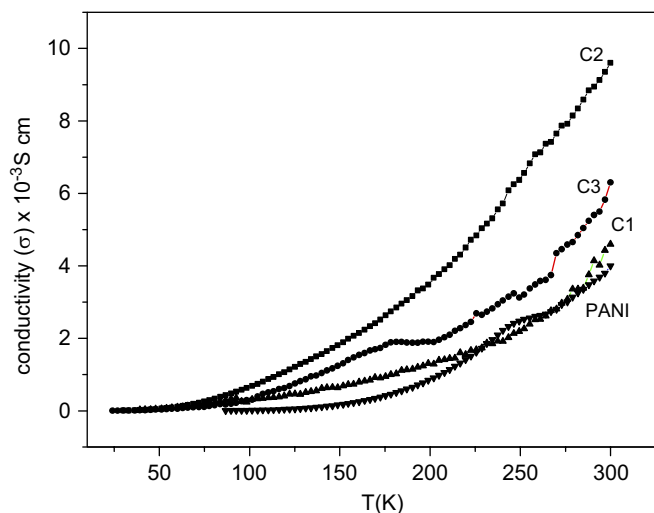


Fig. 5. Temperature dependence of the conductivity of $\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites (C1, C2 and C3). A sample of PANI is also presented.

disorder in the amorphous region. The characteristic Mott temperature T_0 for PANI is $1.98 \times 10^4 \text{ K}$ and increases from 3.0×10^3 to $3.3 \times 10^3 \text{ K}$ and $3.5 \times 10^3 \text{ K}$ for C2, C3 and C1 respectively. These results are consistent with a trend of their room temperature conductivity [21,22].

3. Conclusions

$\text{NiFe}_{1.95}\text{Gd}_{0.05}\text{O}_4$ -PANI composites with different ratio ferrite/PANI have been successfully synthesized by “in situ” polymerization.

The coercivity is approximately the same in all the samples ($75 \times 10^{-4} \text{ T}$) which indicates that the PANI content is not high enough in any of the composites to prevent the interaction among the particles.

It was found that the conductivity at room temperature increases from 4×10^{-3} to $9.6 \times 10^{-3} \text{ S/cm}$ when ferrite content changes from none to 24.5 wt/wt%. A possibility is that the polymerization of PANI coating ferrite nanoparticles induces the conformation change of PANI backbone.

The conductivity of all measured samples decreased with decreasing temperature, exhibiting typical semiconductor behavior.

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