

# Magnetic and electric behavior of NiFe<sub>2</sub>O<sub>4</sub>–PVDF nanocomposites

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NiFe<sub>2</sub>O<sub>4</sub>–PVDF composites in different ratios (10 %, 30 % and 50 %) were prepared in two steps. Firstly, fine nanosized NiFe<sub>2</sub>O<sub>4</sub> powder was synthesized using the precursor solution method. Then the composites were made by hot-press technique. The presence of both the phases (ceramic and polymer) was confirmed by XRD micrographs. The average particle size of the composites varied from 18–23 nm. SEM micrographs showed that the ferrite particles were embedded in the polymer matrix. The saturation magnetization and the remanence showed an increasing trend with the increase in ferrite content while the coercivity remained almost constant. Impedance plot showed the presence of a single semicircle, which indicates the presence of bulk effect. The composites exhibited non-Debye relaxation. The bulk conductivity followed the Arrhenius type of behavior. The conduction mechanism was explained by the Vervey-de-Boer mechanism.

Keywords: nano-composites, magnetization, impedance, conduction, Vervey-de-Boer mechanism

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#### 1. Introduction

The magnetic properties of nanoparticles are a subject of extensive research from the viewpoint of studying their magnetic behavior (size and surface effects), quantum tunneling of magnetization, giant magnetoresistive sensors and ferrofluids. The magnetic properties are strongly dependent on particle size. However, during the processing, agglomeration of nanoparticles takes place, which prevents the material from attaining their full potential in terms of the desirable magnetic response. Thus, the agglomeration, which is one of the main elements in the synthesis of magnetic nanoparticles, is thought to be eliminated by the use of the polymer matrix. Magnetic nano-composites possess unique physical and chemical properties compared to their bulk counterparts. They are considered as an important area of recent research owning to their range of applications in electromagnetic interference shielding, drug delivery, drug targeting and as contrasting agents in magnetic resonance imagining (MRI) [1-3].

Magnetic composites based on ferrites ( $Fe_3O_4$ ) and polymer matrices such as polymethylacrylate [4], polystyrene [5, 6] and polyvinyl alcohol [7–9] have been already reported in the literature.

Nowadays, multiferroic materials, which possess both magnetic and electrical properties, have gained importance from application point of view. These materials offer wide opportunities for potential applications in information storage, such as spintronic devices and sensors, where both electric and magnetic field can be coupled giving enough opportunity for manipulating devices. Keeping this aspect in mind an attempt has been made to prepare nano-composites containing both ferroelectric and ferromagnetic phases. A systematic study on the morphology of mixed metal oxides like NiFe<sub>2</sub>O<sub>4</sub> based polymer composites is rarely found in literature. The ferroelectric phase comprises polymer polyvinyldene fluoride (PVDF) whereas the ceramic phase consists of nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>) powders. The present paper reports the structural, micro-structural, magnetic and electrical properties of NiFe<sub>2</sub>O<sub>4</sub> and PVDF composites in different ratios (10 %, 30 % and 50 %).

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## 2. Experiment

The chemicals used were: nickel ferrite (Merck 99.9 %), ferric nitrate (Merck 99.9 %), triethleyene amine (Merck 99.9 %), ethylene glycol (Merck 99.9 %) and polyvinlydene fluoride (Fluka).

The composites were prepared in two steps: In the first step, nanocrystalline powders of NiFe<sub>2</sub>O<sub>4</sub> were prepared by precursor solution technique. Nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ferrite nitrate  $Fe(NO_3)_2 \cdot 9H_2O$ , triethleyene amine (TEA) were used as starting reagents. The metal nitrates were taken in 1:1 M ratio and dissolved together in a minimum amount of de-ionized water to get a clear solution. TEA was added to the solution and stirred thoroughly. The molar ratio of metal nitrates to TEA was taken as 1:5. Then an ammoniacal solution was slowly added to adjust the pH 7. The mixed solution was heated on a hot plate at nearly 180 °C for complete dehydration. A large amount of gases in the form of nitrates, carbonates, were evolved during the heating. TEA, which acted as a complexing agent played a dual role. It helped in the distribution of cations in the precursor solution throughout the TEA network to prevent selective precipitation during the evaporation process. Furthermore, it also served as a template for the generation of voluminous matrix of polar mesoporous carbon rich precursor mass on oxidation. The mesoporous carbonaceous precursor provided heat by combustion during pyrolysis and facilitated the reduction of the external temperature required for phase formation. The whole mechanism of these reactions has already been discussed [10]. The fluffy mass was calcined at 600 °C to get the desired nanosized ceramic powders. The structural and microstructural characterization of NiFe2O4 ceramics were reported elsewhere [11].

In the second step, nano-composites using polyvinlydene fluoride (PVDF) as the polymer matrix was made. A required amount of PVDF was dissolved in ethyl methyl ketone with the help of a magnetic stirrer till a clear solution was obtained. Then the nickel ferrite powder in the required ratio was mixed in the polymer matrix and continuously stirred. The mixture was further dried to form gel. The gel was hot pressed between the metal discs at a pressure of 10 MPa and a temperature of 200 °C

(311 1200 (6 2 0) -(440 220) (2 2 2) (422) (622) (511) 533) 50% 1000 ntensity (arb unit) 800 600 30% 400 200 10% 0 20 30 40 50 60 70 80 Bragg angle (20)

Fig. 1. XRD pattern of NiFe<sub>2</sub>O<sub>4</sub>–PVDF (10, 30 and 50 %) nano-composites.

to obtain small sheets of composites of  $300-500 \mu m$ . In this way, the nanocomposites of NiFe<sub>2</sub>O<sub>4</sub>–PVDF composites in different weight percentage (10, 30 and 50 %) were prepared. The structural analysis was performed by Seifert D500 X-ray diffractometer using CoK target. Microstructural characterization was done using JEOL-JSM 5800 microscope. The electrical properties of the prepared composites as a function of frequency and temperature were measured with Hioki 3532 LCR meter in a programmable temperature chamber. The magnetization behavior was studied with a vibrating-sample magnetometer.

### 3. Results and discussion

X-ray diffraction patterns of NiFe<sub>2</sub>O<sub>4</sub>–PVDF (10, 30 and 50 %) composites are shown in Fig. 1. The peaks were matched well with the JCPDS (10-0325) file and the peak positions of NiFe<sub>2</sub>O<sub>4</sub> have been marked. The presence of PVDF was also confirmed by the occurrence of a single peak marked in the figure. Thus the formation of both (ceramic and polymer) phases was confirmed by the diffraction patterns. It was observed that with the increase in the percentage of ceramic powders in the composites, the peak of PVDF disappeared. The broad diffraction lines exhibited by the composites are indicative of the fine particle nature. A rough estimation of the crystallite size was carried out using the Scher-

rer equation. The correction for the instrumental broadening with respect to the standard silicon was calculated using the equation:

$$\beta_p^2 = \beta_{obs}^2 - \beta_s^2 \tag{1}$$

where  $\beta_p$  is the FWHM of the particle and  $\beta_s$  is the FWHM of standard silicon.

After applying the correction for instrumental broadening it was stated that the peak width analysis of the major peaks of the XRD pattern corresponded to an average crystallite size. The particle sizes calculated for 10 %, 30 % and 50 % NiFe<sub>2</sub>O<sub>4</sub>–PVDF on the basis of the analysis, were 21 nm, 18 nm and 25 nm respectively. The small variation in the particle size may be caused by the agglomeration of the ferrite powders when dispersed in the polymer matrix.

Fig. 2 depicts the microstructures of the prepared composites, taken with a scanning electron microscope. The microstructural characterization in the present study supports the long-range propagation of a woven network of PVDF microtubules formed by the cross linking of the polymeric carbon chain. On the surface of the nanocomposite, numerous voids are present which are caused by the matrix cavitation due to the addition of the nanoparticles. The29 voids may contain particles inside and these particles serve as a nucleating agent, which changes the morphological structure of the PVDF matrix. Secondly, the nanoparticles act as stress concentrator which promotes cavitation at the particle polymer boundaries.

The magnetization curves obtained at room temperature for the base material (NiFe<sub>2</sub>O<sub>4</sub>) and the composite (NiFe<sub>2</sub>O<sub>4</sub>–PVDF (50 %)) are plotted in Fig. 3. The prepared nickel ferrite, which was the base material, revealed its saturation magnetization of 46.0 emu/g which was close to the theoretical value of 50 emu/g reported for bulk nickel ferrite [12]. The slightly lower value of the present nanoferrite may be attributed to its lower particle size. The finer ferrite particles exhibit different magnetization behavior in their core-shell regimes whereby the core magnetic moments are the ones to be aligned initially followed by the moments in the surface layer that behave as spin glass [13]. Dominant spin

glass behavior in the present nanoferrite is caused by its large surface area that lowers the saturation magnetization compared to bulk nickel ferrite. The magnetization value increased with the addition of PVDF suggesting a correlative dependence of  $M_s$ with ferrite densification on the filler material, *i.e.* PVDF. Such densification was also supported by a relative increase in remanence  $(M_r)$  value with the ferrite content in the polymer-bonded composites as shown in Fig. 4. Higher volume fraction of ferrite nanoparticles reduced the demagnetization effects leading to an increase in  $M_r$ . However, it is interesting to note that the coercivity of the samples containing ferrite in the polymer bonded composites remained almost unchanged. This suggested that coercivity was more dependent on the domain orientation in the nanoferrite particles as compared to any ferromagnetic exchange amongst the particles in the ceramic-polymer composite samples. This was also supported by the fact that the particle sizes were nearly the same in all the composites. The coercivity  $(H_c)$  value of the nanocomposites was much higher compared to that of base nickel nanoferrite (Table 1). The increased densities of voids in the composites impede domain wall motion thereby increasing the coercivity in a high nickel ferrite (50 %) polymer-bonded sample. However, such high coercivity value in polymer-bonded composites can also be attributed to the stress generated in the ferrite nanoparticles during hot pressing to get the composite sheets. Macro-scale dependence of ferrite volume fraction closely followed the saturation magnetization whereby 50 % composite showed nearly half of the  $M_s$  value compared to the base nanoferrite (Table 1).

The impedance (*Z*) was recorded as a function of frequency (100 Hz to 5 MHz) at different temperatures. The variations of real (*Z'*) and imaginary (*Z''*) part of the impedance of NiFe<sub>2</sub>O<sub>4</sub>–PVDF (50 %) at different temperatures are shown in Fig. 5. At low temperature only an arc appears which takes the shape of a semicircle at higher temperature. In general, whether a full, partial or no semicircle is observed depends on the strength of the relaxation and the experimentally available frequency range. The intercept of the semicircular arc along *Z'* axis (*i.e. X*-axis) gives the value of the bulk resistance. It



Fig. 2. SEM micrographs of NiFe<sub>2</sub>O<sub>4</sub>-PVDF (10, 30 and 50 %) nano-composites.

Table 1.	Magnetization parameters of different nickel ferrite and nickel ferrite-polymer
	bonded composites.

Nickel ferrite content	Sat. magn,	Remanence,	Coercivity,	%
(%) + PVDF	$M_s$ , (emu/g)	$M_r$ , (emu/g)	$H_c$ (Gauss)	Magnetization
10 %	4.09	1.29	165.45	9.0
30 %	14.86	4.53	164.92	32.0
50 %	23.18	7.43	165.92	50.0
Base (without polymer)	46.0	7.06	93.13	_

is observed that these curves do not coincide with the origin hence, there is a series resistance  $R_s$  that can be ascribed to the LCR circuit representation (Inset) of the compound [14]. It was observed that only one semicircle is present at higher temperature. But the tail which appeared at 200 °C may be the origin of the second semicircle that can be obtained only when the measurement frequency range is further lowered. This first semicircle, which may be ascribed to a parallel combination of bulk resistance,  $R_b$  and  $C_b$ , corresponds to the grain properties of the material. Similar trend was observed for all the composites. The dielectric relaxation in the system can be assessed through complex impedance plots. For Debye type relaxation, the center of the semicircle should be located on the Z' axis, whereas for non-Debye type relaxation these argand plane plots are close to semicircular arcs with the end-points on the real axis, and the center below the axis [15]. This decentralization or non-Debye type relaxation obeys Cole–Coles formalism where the depressed semicircle represents typically a phenomenon with



Fig. 3. Magnetization plots of NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>– PVDF (50 %) nano-composites.



Magnetising Field (kG)

Fig. 4. Magnetization plots of NiFe<sub>2</sub>O<sub>4</sub>–PVDF (10, 30 and 50 %) nano-composites.

a spread of relaxation time. The complex impedance in such situation can be described as:

$$Z^*(\boldsymbol{\omega}) = \frac{R}{1 + (j\boldsymbol{\omega}/\boldsymbol{\omega}_o)^{1-n}} \tag{2}$$

where  $\omega$  is the angular frequency. The exponent *n* represents the magnitude of the departure of the electrical response from an ideal condition, which has a single relaxation time and when the exponent n assumes the value zero, (*i.e.* 1 - n = 1), the above

equation gives the classical Debyes formalism This non-ideal behavior is correlated to several factors such as the grain size distribution, grain orientation, grain boundaries *etc*. In other words, *n* gives further representation of the distribution of the relaxation times. The existence of the distribution of relaxation times is correlated to some depression degree ( $\beta$ ), which is related to (*n*) by the following equation:

$$n = 2\beta/\pi \tag{3}$$

The absence of a second and third semicircle in Fig. 5 reveals that the contribution of grain boundary and the electrode-material interface to the impedance are negligible within this frequency range.

The hopping conduction mechanism is generally consistent with the existence of a high density of states in the materials having a band gap like that of a semiconductor. Due to the localization of charge carriers, formation of polarons takes place and hence hopping may occur between the neighboring sites. Fig. 6 shows the variation of bulk conductivity versus reciprocal of T. The bulk conductivity was obtained from the intercept of the arcs in the Z''axis (Fig. 5) and evaluated from the impedance data using the relation:

$$\sigma_{dc} = \frac{t}{R_b A} \tag{4}$$

where  $R_b$  is the bulk resistance, t the thickness and A the area of the electrode deposited on the sample. The conductivity of all the measured samples decreased with increasing temperature, exhibiting typical semiconductor behavior. The data were best fit to the relationship

$$\sigma = A \exp(-E_a/kT) \tag{5}$$

where  $E_a$  represents the activation energy,  $\sigma$  the conductivity at temperature T, A a temperature independent constant and k the Boltzmann constant [16, 17]. The value of the activation energy (Table 2) was calculated from the slope of the graphs. The electrical conductivity in Ni-ferrites can be explained by the Vervey-de-Boer mechanism in which electron exchange between ions of the same element present in more than one valence state takes place. Such



Fig. 5. Impedance plot of NiFe<sub>2</sub>O<sub>4</sub>–PVDF (50 %) at two highest temperatures recorded (170 °C and 200 °C).



Fig. 6. d.c. bulk conductivity plot of NiFe<sub>2</sub>O<sub>4</sub>–PVDF (10, 30 and 50 %) composites as a function of  $10^3/T$ .

ions are distributed randomly over crystallographically equivalent lattice sites. There is a possibility of reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> at elevated temperatures [18, 19]. Again Ni<sup>3+</sup> ions can be formed when ferrites are cooled down from the firing temperature, due to absorption of oxygen ions. These electron exchange processes between ions of the same element Fe<sup>3+</sup>  $\rightleftharpoons$  Fe<sup>2+</sup> and Ni<sup>3+</sup>  $\rightleftharpoons$  Ni<sup>2+</sup> are responsible for the variation of conductivity. The presence of carbon ions in PVDF does not participate in the conduc-

Table 2. Electrical parameters of the composites.

Nickel ferrite content	Conductivity,	Activation
(%) + PVDF	$\sigma_{dc} (\mathrm{Scm^{-1}})$	energy, $E_a$ (eV)
10 %	4.93 E-6	0.021
30 %	1.22 E-6	0.019
50 %	5.37E-6	0.078

tion process but they limit the degree of conduction by blocking up the  $Fe^{2+} \Longrightarrow Fe^{3+}$  transformation. This phenomenon might hinder the Vervey-de-Boer mechanism resulting in the decrease of conductivity with an increase in polymer percentage (Table 2).

#### 4. Conclusions

NiFe<sub>2</sub>O<sub>4</sub>–PVDF nano-composites with different weight ratios (10, 30 and 50 %) were prepared by hot press technique. The presence of both ceramic and polymer phase was confirmed by XRD micrographs. NiFe<sub>2</sub>O<sub>4</sub> nanoparticles exhibited saturation magnetization slightly lower than the bulk material, which may be due to the dominant spin glass behavior. The increase in the percentage of ferrite particles reduced the demagnetization effect, which led to the increase in the value of remanent magnetization. The coercitivity value remained the same for all the nano-composites, which suggested that it was mainly dependent on the domain reorientation in the nanoferrite particles. The conductivity value decreased with the increase in the polymer percentage as PVDF hindered the Vervey-de-Boer mechanism.

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