Optimising piezoelectric and magnetoelectric responses on $CoFe_2O_4$/P(VDF-TrFE) nanocomposites

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Magnetoelectric nanocomposite films composed of magnetostrictive $CoFe_2O_4$ nanoparticles with sizes between 35 and 55 nm embedded in P(VDF-TrFE) have been successfully prepared by a solvent casting method. The ferroelectric, piezoelectric, magnetic and magnetoelectric properties of the nanocomposite and their variation with the wt% of the ferrite filler, thickness of the composite and direction of the applied magnetic field have been investigated.

Ferroelectric and piezoelectric properties are improved when small amount of ferrite nanoparticles were added to the polymeric matrix. Magnetic properties vary linearity with ferrite content. The highest magnetoelectric response of 41.3 mV/cmOe was found in the composite with 72wt% when a 2.5 kOe DC field was transversely applied to the sample surface. This value is among the highest reported in two phase particulate polymer nanocomposites. Thickness of the composite has no influence in the magnetoelectric response, allowing tailoring sensor thickness for specific applications. The good value of the magnetoelectric coefficient and the flexibility of the films make these composites suitable for applications in magnetoelectric smart devices.

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1. Introduction

Magnetoelectric (ME) and multiferroic materials with coexistence of at least two ferroic orders (ferroelectric, ferromagnetic or ferroelastic) have attracted increasing attention due to their potential device applications in areas such as data storage, switching, modulation of amplitudes, polarization and filters, waveguides, sensors, transducers and spin wave generation, among others [1-4]. One of the most promising ideas is that magnetoelectric bits may be used to store information both in the magnetization and polarization . This type of encoding information in such four-state memory has recently been demonstrated [5-6].

In single phase multiferroics the magnetic and ferroelectric orders frequently occur largely independent of each other and as a result the magnetoelectric coupling tends to be very small or occurs at temperatures too low for practical applications [3], [7]. On the other hand, and with larger design flexibility, multiferroic ME composites fabricated by combining piezoelectric and magnetostrictive materials have drawn significant recent interest due to their multifunctionality, in which the coupling interaction between the piezoelectric and magnetostrictive phases produce a large ME response [8]. Due to their technologically viable ME response, different ME composites have been investigated in recent years, including multilayer and particulate composites[3].

So far, three main types of bulk magnetoelectric composites have been investigated both experimentally and theoretically: a) magnetic metals/alloys e.g., laminated Terfenol-D and Metglas and piezoelectric ceramics; b) laminated Terfenol-D and Metglass and piezoelectric polymers; c) particulate composites of ferrite and piezoelectric ceramics e.g., lead zirconate titanate [3].

The ME coefficients obtained in ceramic particulate or laminated composites are typically three orders of magnitude higher than in single phase materials [9-10]. Ceramic composites, on the other hand, may become fragile and are limited by deleterious reactions at the interface regions leading to low electrical resistivities and high dielectric losses >0.1, hindering in this way the incorporation into devices of these materials [11].

Another promising and less explored approach to obtain a good ME coupling is the development of particulate composites of Terfenol-D and PZT within a polymer matrix [12]. Such composites can be easily fabricated by conventional low-temperature processing methods into a variety of forms such as thin sheets and moulded shapes. The simplest three-phase ME composite is a quasi 0-3 type particulate composite where Terfenol-D grains are randomly oriented in a matrix of PZT and polymer. The incorporation of PZT into the polymeric matrix makes the composite more brittle [12-13] and although Terfenol-D has the highest magnetostriction amongst all known materials, this rare-earth iron alloy is quite costly and very brittle.

One way to avoid some of the aforementioned problems related to the use of ceramics and to obtain magnetoelectric composites with high magnetoelectric coupling is the use polymer based composites, where the polymer matrix is the piezoelectric phase.

Poly(vinylidene fluoride) (PVDF) and copolymers have the best electroactive performance in the small class of polymers displaying piezo, pyro, and ferroelectricity. These properties are originated from the strong molecular dipoles within the polymer chains [14]. From the four crystal modifications known for PVDF, denoted as α, β, γ and δ, the highest piezo-, pyro- and ferroelectric properties are associated to the β-phase.

Poly(vinylidene fluoride/trifluoroethylene) P(VDF-TrFE) copolymers, containing VDF between 55 and 82 mol%, have been widely studied for their interesting ferroelectric properties. Besides the pyro- and piezoelectric activities of PVDF, those copolymers exhibit a ferro- to paraelectric phase transition at a temperature Tc which is below the melting temperature of the material and whose value increases with increasing VDF mol% content. Contrary to the PVDF homopolymer, when crystallized from the melt these copolymers present the ferroelectric phase, which is an essential factor for the preparation of ME composites [15-16].

Piezoelectric properties of PVDF polymers and co-polymers, that strongly influence the ME response are dependent of the experimental processing conditions [17-18].

Preliminary studies on multiferroic nanocomposite films composed of P(VDF-TrFE) and $CoFe_2O_4$ nanoparticles have been conducted in films prepared by a complex processing method involving vacuum treatment [19]. This study shows the potential of these composites for magnetoelectric applications but effect of low ferrite concentrations in the ferroelectric, piezoelectric and magnetic responses was not been reported. Further, the effect of magnetic field direction and the composite thickness in the magnetic and magnetoelectric response also needs to be addressed in order to obtain suitable materials for useful applications.

In this work PVDF-TrFE/$CoFe_2O_4$ magnetoelectric composites prepared by a simplified solvent casting method without vacuum treatment have been investigated addressing the aforementioned issues. Further, the size of the nanoparticles is half of the ones used in [19], looking for a larger interaction area between the piezoelectric and magnetostrictive phases.

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2. Experimental

$CoFe_2O_4$ nanoparticles were purchased from Nanoamor with dimensions between 35-55 nm. The synthesis of this kind of nanoparticles is well discussed in the literature [20-22]. *N,N*-dimethylformamide (DMF, pure grade) was supplied by Fluka and P(VDF-TrFE) was supplied by Solvay Solexis. All the chemicals and nanoparticles were used as received from the suppliers.

For composite preparation, the desired amount of nanoparticles was added to DMF and then placed in ultrasound bath during 8h to ensure that nanoparticles were well dispersed in the solution and also to avoid loose aggregates [23]. Then P(VDF-TrFE) powder was subsequently added.

Further, the obtained mixture was placed in a Teflon mechanical stirrer with ultrasound bath for complete dissolution of the polymer during 2h. Flexible films were obtained by spreading the solution on a clean glass substrate. Solvent evaporation and polymer crystallization were performed inside an oven at controlled temperature. The samples were maintained inside the oven for 10 min at 210 ºC. Crystallization was achieved by cooling down the samples to room temperature. The content of ferrite nanoparticles varied from 3 to 80 wt% (0.01 to 0.59 in volume fraction) and the thickness of samples was controlled to be approximately 25, 50 and 75μm.

The ferroelectric hysteresis loops of the composites were measured at room temperature using Radiant Ferroelectric Premier II LC equipment. After 30 minutes of corona poling at 120ºC in a home-made chamber, the piezoelectric response (d_{33}) of the poled samples was analyzed with a wide range d_{33}-meter (model 8000, *APC Int Ltd*).

Magnetic hysteresis loops at room temperature were measured using a vibrating sample magnetometer (Oxford Instruments) up to a maximum field of 1.8 T.

In order to obtain the out of plane and in plane magnetoelectric coefficient α_{33} and α_{31} respectively, *dc* (bias) and *ac* magnetic fields were applied simultaneously in two directions: along the same direction that the electric polarization of the P(VDF-TrFE), that is, perpendicular to the composite´s surface and also parallel to the composite´s surface . The *ac* driving magnetic field was provided by a pair of Helmmholtz coils, being its amplitude of 8.1 mOe at 5 kHz. The external bias field was provided by an electromagnet with a maximum value of 1.2 T. The induced magnetoelectric voltage in the samples was measured by using a Standford Research Lock-in amplifier.

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3. Results and Discussion

The ferroelectric hysteresis loops of the composites with the different ferrite weight fractions as well as for a given weight fraction for different thicknesses are presented in figure 1a and figure 1b, respectively.

The ferroelectric properties were tested under an electric field with a maximum strength of 900 kV/cm. In figure 1b it is possible to observe that nanocomposite thickness has no influence in the ferroelectric response of the samples, neither in the spontaneous polarization nor in the coercive field. This important fact is contrary to what is observed in other ferroelectric systems, in particular in composites in which the domain reversal within the films is changed due to the variations in the distribution of the filler in composites of different thickness [24].

All samples exhibit saturated hysteresis loops and the maximum polarization reaches a value of 18.1 $\mu C/cm^2$ with a filler content of 7 wt%. Increasing ferrite concentration to higher values will cause a drop in the maximum polarization value. This enhancement in the maximum polarization value of polymer/ferrite nanocomposites for low loading contents has been reported previously [25]. Two main effects can be on the basis of this phenomenon: on the one hand ferrite nanoparticles may introduce additional free charges required to compensate and stabilize the polarization domain, on the other hand nanoparticles can act as heterogeneous nucleation centers for ferroelectric domains during the polarization [26]. Moreover, large interfacial areas in the composites containing nanometer scale fillers promote the exchange coupling effect through a dipolar interface layer and results in higher polarization levels and dielectric responses [27]. From ferrite contents higher than 19.5 wt%, the maximum polarization decreases in comparison with the pure polymer, indicative of the existence of a critical point for the maximum ferrite content optimizing the ferro- and piezoelectric polymer response. At this concentration, the long-range ordered dipole ordering of the polymer chains is destroyed and the polarization decreases significantly due to the fact that nano-sized ferrite particles hinder domain wall movement [25].

It was also observed an increase of the coercive field with increasing ferrite content until a value of 62.1 wt%. Increasing concentration from this value results in a sharp decrease in the coercive field of the nanocomposites.

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The dependence of the maximum polarization and coercive field values with ferrite content is represented in figure 2a. Figure 2b illustrates the correlation between the remnant polarization and piezoelectric response of the composites. As ferrite concentration increases, both quantities increase until a maximum value of 16.3 $\mu C/cm^2$ and 27 pC/N respectively at a concentration of ~ 7wt% content. For higher concentrations, the values of both remnant polarization and piezoelectric response decrease, being this decrease stronger for concentrations above 60%wt ferrite. In this way, the presence of small quantities of the magnetostrictive phase in the composite significantly improves the piezoelectric and polarization responses of the copolymer matrix, demonstrating that those nanocomposites are promising candidates for room temperature piezoelectric and ferroelectric applications. On the other hand, as demonstrated later, larger magnetostrictive phase than 7 wt% is needed in order to obtain suitable magnetoelectric coupling.

The good ferroelectric and piezoelectric properties of $CoFe_2O_4$/P(VDF-TrFE) nanocomposites are intimately related to the uniform dispersion of the ferrite nanoparticles [19]. The experimental results confirm that the presence of the nanoparticles significantly influence the polarization and piezoelectric responses of the copolymer matrix, in particular for low ferrite concentrations [28]. It has been reported that cobalt ferrites interact with the PVDF homopolymer matrix in order to favor the crystallization of the electroactive β- phase, which has a polar-all-*trans* conformation, with respect to α phase, which shows *trans*-gauche molecular conformation [23], i.e. Co nanofillers favor the polar phase of the polymer. Analogously, low nanofiller concentration in the co-polymer matrix may favor arrangement of the polar conformations and therefore the increase of the ferroelectric and piezoelectric responses.

The saturation magnetization of a powder sample of $CoFe_2O_4$ nanoparticles is over 60 emu/g. Saturation magnetization values of the ferrite particles within the polymer matrix fit well to that value when the loops are normalized with the concentration of magnetic particles in the composites. The shape of the measured loops demonstrates that magnetic particles are randomly oriented within the polymer matrix (figure 3).

For all composites a coercive field of 0.21 T was measured, higher than the measured one in similar nanocomposites prepared by other methods.[19]. It was found that the thickness of the nanocomposite films and the direction of the magnetic field (in plane and out of plane) has no influence in the magnetic response of the nanocomposites, demonstrating that the experimental procedure used to prepare the samples does not affect the isotropy of the films.

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Figure 4a shows the variation of the ME voltage coefficient with the DC magnetic field for the different ferrite concentrations, measured under an AC field of 1 Oe with a 5 kHz amplitude.

It can be observed that the induced voltage increases with increasing DC magnetic field until a maximum of 41.3 mV/cmOe at a magnetic field of 2.5 kOe. With further increase of the DC magnetic field a decrease in the induced voltage is observed.

The differences of the in plane (magnetization parallel to the polarization) and out of plane (magnetization perpendicular to the polarization) can be observed in figure 4b.

The ME coefficient is three times higher in the out of plane measurement, which is fully to be attributed to the difference in the d_{33} and d_{31} piezoelectric constants of the polymer, since no difference is detected in the in plane and out of plane magnetic response of the nanocomposite [29] (see figure 3b).

As can be seen in figure 4c and as expected for well dispersed composites [30-31] no difference is noted in the ME response when composite thickness and AC applied field are changed. In this way, it can be concluded that the residual stress status of the composites, that strongly depends on film thickness and deeply affects the ME coupling, together with preferential nanoparticle orientation and interface defects [32], does not play a significant role in the processed composites.

Figure 4d shows the ME response of the nanocomposites at a bias field of 2.5 kOe for increasing $CoFe_2O_4$ loading. The initial increase in the ME voltage is explained by the increase of the magnetosctriction due to the substantial increase the magnetostrictive phase. This response is optimized at 72 wt% $CoFe_2O_4$ content. For higher concentrations, nanoparticles lead to the disruption of the ferroelectric copolymer phase [19], having as a result an abrupt decrease in the ME response of the nanocomposite. The theoretical fitting of this behavior was performed by using the model presented in [30-31]. In this model, the ME response α_{33} can be expressed as:

$$\alpha_{33} = (1-\phi)\frac{L_E}{\varepsilon}\left(d_{31p}\frac{dY_{xp}}{dH_m} + d_{32p}\frac{dT_{yp}}{dH_m} + d_{33p}\frac{dT_{zp}}{dH_M}\right)\left(\frac{dH_m}{dH}\right) \quad , \qquad (1)$$

where L_E and $\frac{dH_p}{dH}$ are given by:

$$L_E = \frac{[\varepsilon_m + 2\varepsilon_p]}{[(1-\phi)\varepsilon_m + (2+\phi)\varepsilon_p]} \qquad (2)$$

$$\frac{dH_p}{dH} = \frac{3\xi_p}{(1-\phi)\left(\xi_m + \frac{dM_m}{dH_m}\right) + (2+\phi)\xi_p} \qquad (3)$$

Here, p and m indicate the polymer and magnetic phase respectively; d_{3n} the piezoelectric coefficients; ε the dielectric constant, ϕ the volume fraction of the magnetostrictive phase; T and H are the stress and applied magnetic field, respectively; ξ the magnetic permeability and M the magnetization. $\frac{dM_m}{dH_m}$ is obtained from the magnetization curve (figure 3).

As expected and predicted by the theory, the good value of piezoelectric coefficient reached at 7wt% is not enough to obtain a good magnetoelectric coefficient in samples with low magnetostrictive nanoparticle concentrations since it is necessary a substantial presence of both ferroelectric and magnetostrictive phases [8, 33]. The optimal compromise is obtained for filler concentrations of 72 wt%.

Finally the significant discrepancy between the theoretical and experimental values in the highest concentrated sample is due to the fact that for these high nanoparticle loadings, filler dispersion cannot be properly achieved. Therefore, this large amount of magnetostrictive phase leads to the disruption of the polymer microstructure and of the ferroelectric properties in the multiferroic nanocomposite [19].

4. Conclusions

Magnetoelectric nanocomposites were successfully produced using as piezoelectric phase PVDF-TrFE and as magnetostrictive phase $CoFe_2O_4$ nanoparticles by a simple solvent casting method. The resultant multiferroic films exhibit saturated hard magnetic properties and a magnetoelectric coefficient dependent on the loading of the magnetrostrictive phase. The presence of low content of nanoparticles in the composite significantly improves the polarization and piezoelectric responses of the copolymer matrix, demonstrating that low filler content $CoFe_2O_4$/PVDF-TrFE nanocomposites are promising candidates for room temperature piezoelectric and ferroelectric applications. The magnetoelectric response of the material is maximized for 72 wt% filler contents, with a α_{33} value of 41.3 mV/cmOe. Since the value is among the highest reported in particulated polymer nanocomposites, this work provides a promising way to produce flexible magnetoelectric materials to be applied in smart devices.

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Figure captions/numbering

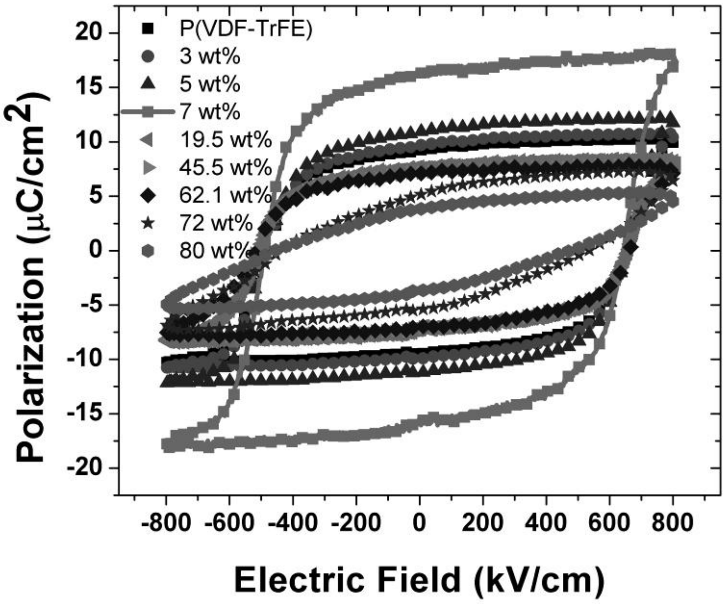

Figure 1(a) Weight fraction-dependent ferroelectric hysteresis loops for $CoFe_2O_4$/P(VDF-TrFE) nanocomposites.

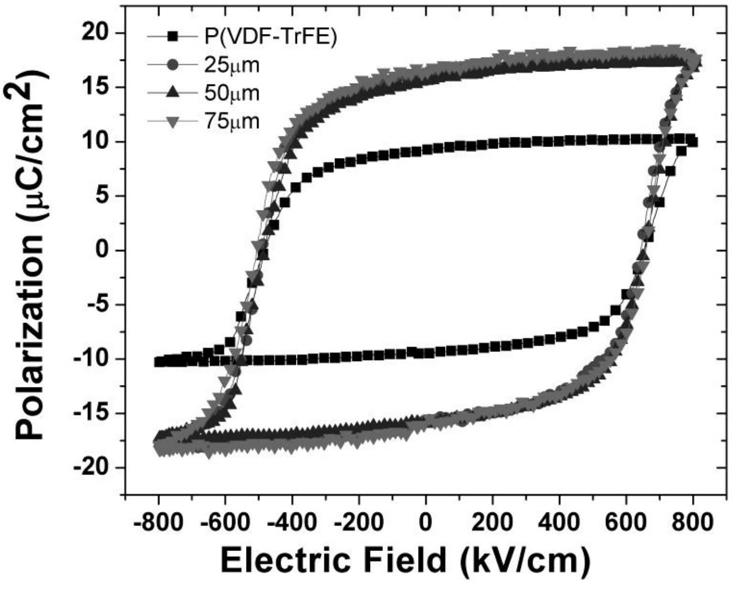

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Figure 1 (b) Ferroelectric hysteresis loops for nanocomposites with the weight fractions of 7% for different polymer thicknesses (25µm, 50µm and 75µm) and for pure P(VDF-TrFE).

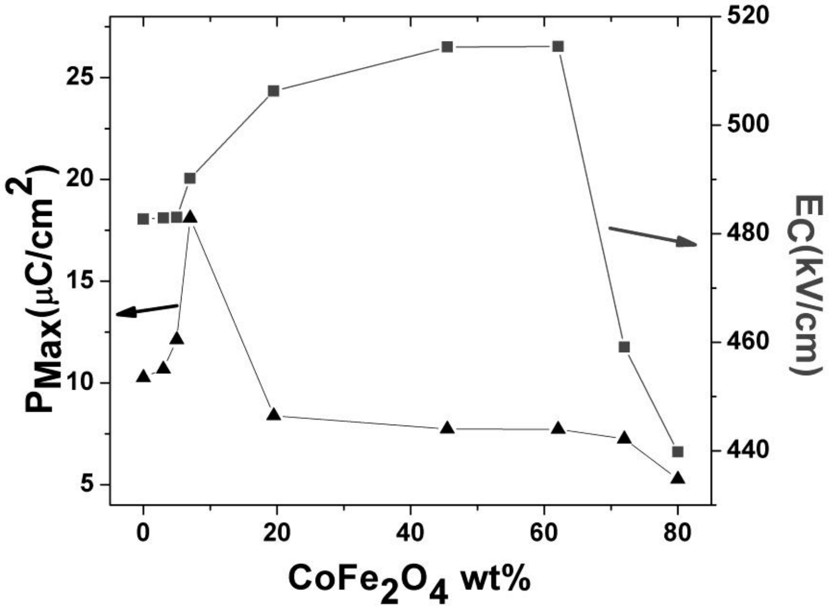

Figure 2. (a) Weight fraction-dependent Maximum Polarization ($P_{Máx}$) and Coercive Electric Field (E_C) of $CoFe_2O_4$/P(VDF-TrFE) nanocomposites

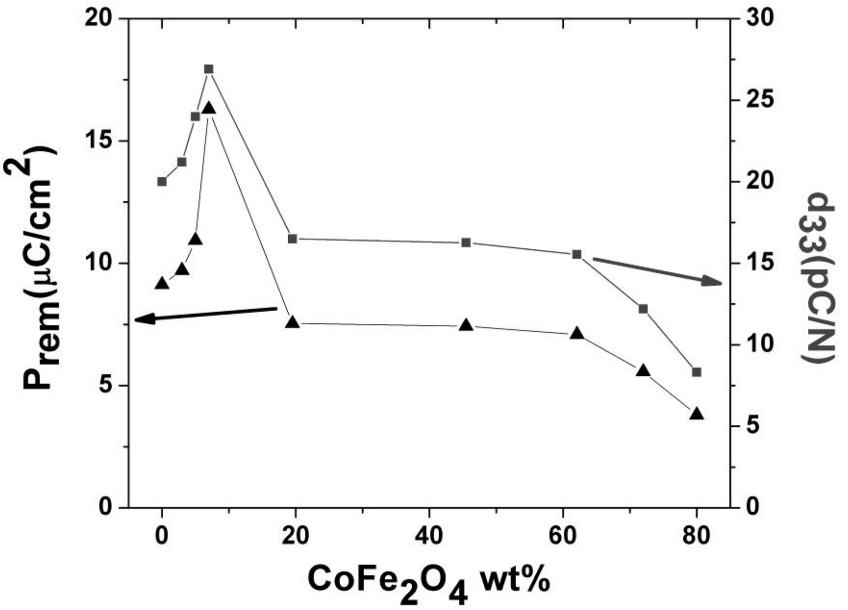

Figure 2. (b) Weight fraction-dependent Remnant Polarization and Piezoelectric Constant (d_{33}).

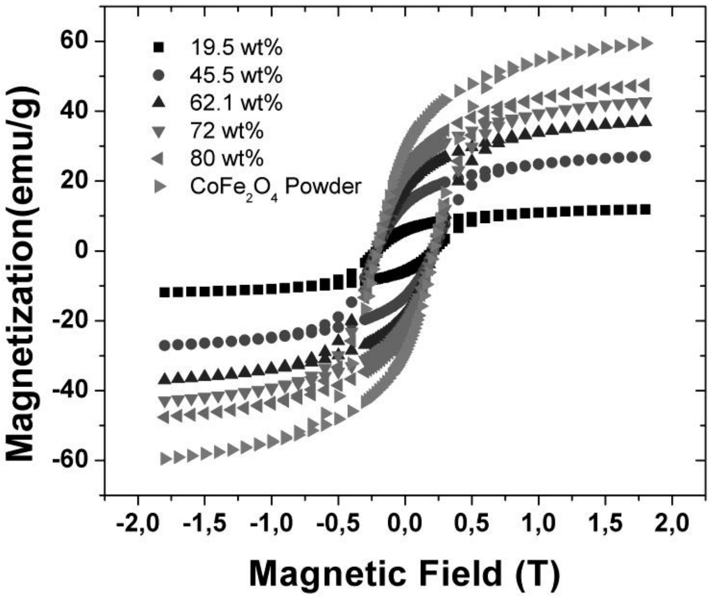

Figure 3. (a) Room temperature hysteresis loops for the pure ferrite nanoparticle powder and for $CoFe_2O_4$/P(VDF-TrFE) nanocomposites.

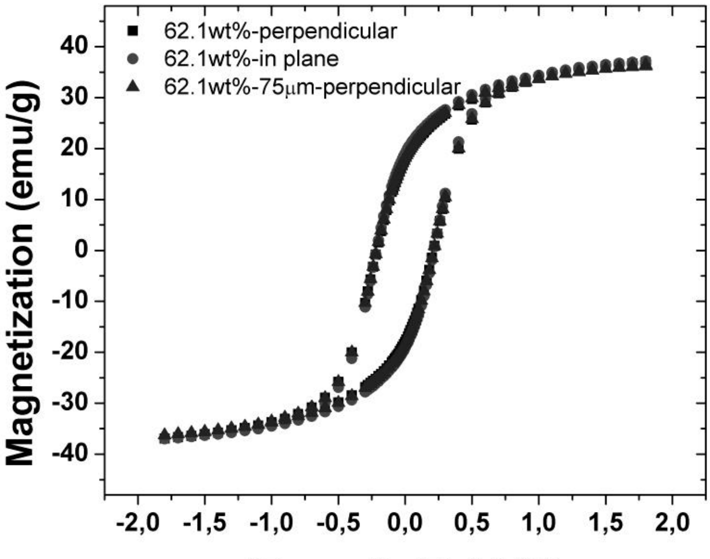

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Figure 3. (b) Room temperature hysteresis loops measured for the composite with 62.1wt% of ferrite for different field directions.

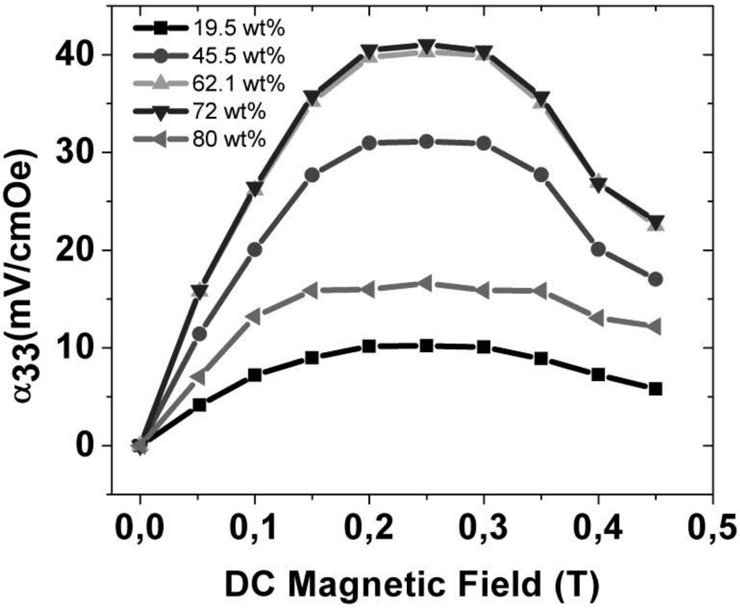

Figure 4. (a) ME coefficients as a function of the bias field and filling fractions of $CoFe_2O_4$ nanoparticle.

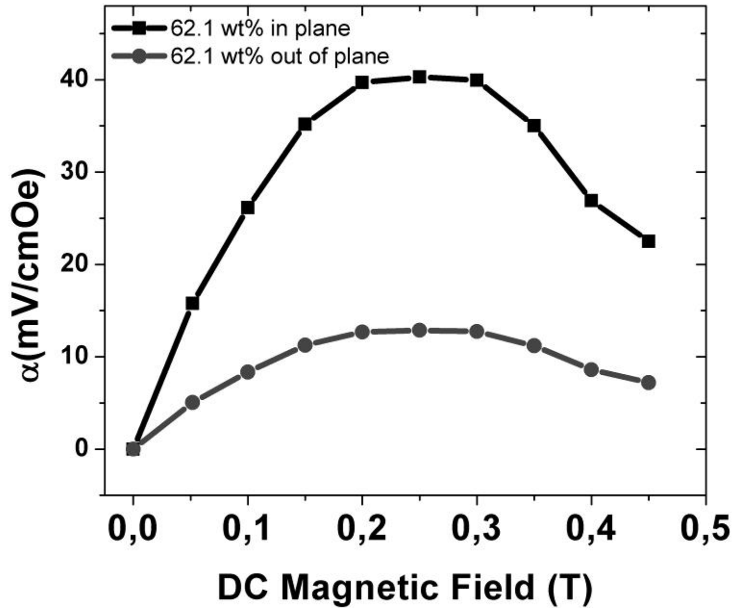

Figure 4. (b) In plane and out of plane ME response of 62.1 wt% ferrite content samples.

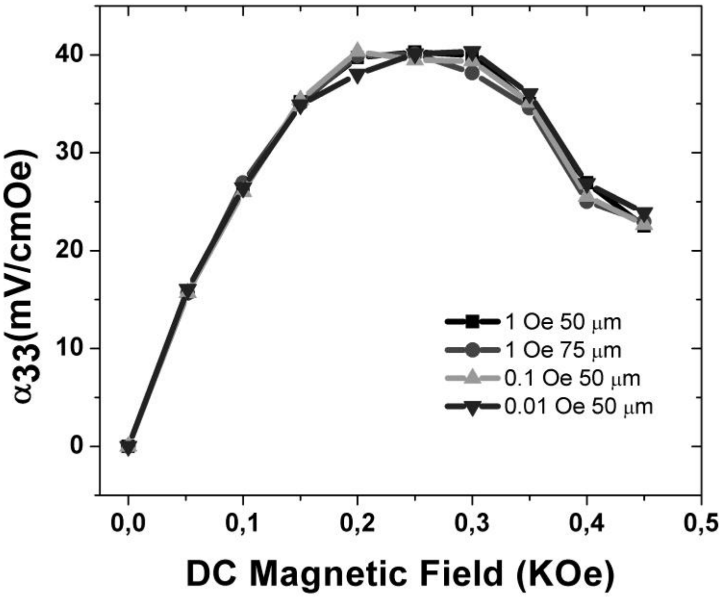

Figure 4. (c) Influence of thickness and AC field in the ME response of 62.1 wt% ferrite content samples.

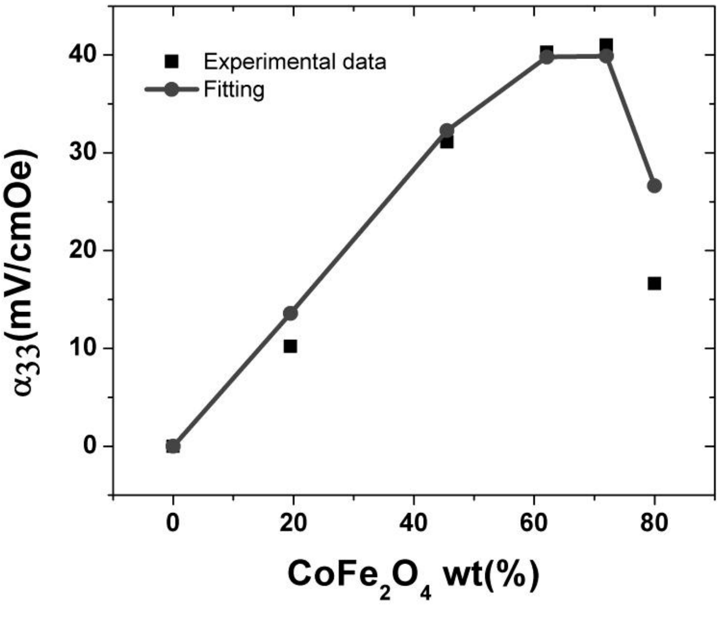

Figure 4. (d) ME coefficients of nanocomposite with different $CoFe_2O_4$ contents at a DC magnetic field of 2.5 kOe.

Optimising piezoelectric and magnetoelectric responses on $CoFe_2O_4$/P(VDF-TrFE) nanocomposites