The shape factor influence on the control process of multiferroic nanoparticle configurations in GHz range

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Abstract. Materials with piezoelectric properties associated with the ferroic phases generate multiferroic structures at microscopic level. Multiferroic core-shell nanoparticles with different configurations were considered: nanospheres versus nanotubes – spherical (magnetostrictive core / piezoelectric shell), respectively cylindrical (magnetostrictive rod / piezoelectric cylindrical coating). The external sphere diameter / cylinder lengths were of 80 – 100 nm to 360 nm, while the inner sphere / rod diameters were of 20 to 60 nm. The influence of the constituents shape on their control process realized by an applied magnetic field, \( H_0 \) (100 – 270 Oe) was investigated. The nanoparticles were simulated using the HFSS 13.0 program, at frequencies in microwave range (16 – 28 GHz), considering the nanostructures with hexaferrites as magnetic phase (\( \text{AFe}_12\text{O}_{19} \)) M-type hexaferrites, with A an alkali earth metal) and the \( \text{Bi}_2\text{NiMnO}_6 \) perovskite like piezoelectric. The particle configurations response is function of their geometrical shape, modified by the core diameter and the shell thickness. The magnetoelectric (ME) coefficient tensor has been determined using a physical algorithm based on the near-filed values in the particles vicinity, generated by the HFSS, and also the ME voltage coefficient (obtained of tens of mV/cm·Oe). Performance of the two shapes composite nanoparticles to generate a strong ME response was discussed comparatively and the influence of the shape factor was illustrated on graphs. Each composite configuration presents specific advantages in respect with the control process by the \( H_0 \) field, considering that the effect of dipolar field generated as response by the electric phase is strongly anisotropic. These features can be elegant illustrated by simulations (non destructive, applied at nanoscale) which help us to decide to the proper nanoparticles shape and the optimal intensity of the applied fields for the desired strength of the ME effect in a defined microscopic area.

1. Introduction

Multiferroic materials with multiple ferroic phases can be obtained using different constituents, in a specific configuration. The core – shell configurations of nanoparticles have demonstrated high values of the magnetoelectric coefficients due to the strong coupling between magnetic and electric phases, mediated by a strain at the certain boundaries between the shell and the core. The shape factor influences consistently the internal processes and consequently the composite properties. The specific quantities control via the shape factor is a method of multiferroic structure optimization which can be easily experimented in practice via simulation. The 3D microscopic model of the composite, realized...
at crystalline lattice level, can be modified non-destructive in order to improve the structure electromagnetic performances. Based on the models given in literature [4, 5], nanoparticles grouped in core-shell nanospheres versus nanotubes have been simulated in this paper in a static magnetic field, applied for polarization.

Application of the ME structures manufactured in such manner are multiple: voltage tunable multiferroic RF/microwave devices, devices with strong converse ME coupling, used at: tunable bandpass filters, high power phase shifters, magnetic sensors, spintronics, energy harvesters, etc.

2. Theoretical considerations

The free energy of a magnetoelectric material, placed in the electric $\vec{E}$ and magnetic $\vec{H}$ fields, can be written as [1]:

$$F(E, H) = F_0 - P_i' E_i - M_i' H_i - \frac{1}{2} e_{ij} E_i E_j - \frac{1}{2} \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} E_i E_j H_k - ...$$

(1)

where $P'$, respectively $M'$ is the spontaneous electric, respectively magnetic polarization, $\varepsilon$ respectively $\mu$ is the electric permittivity, respectively magnetic permeability tensor, $\alpha$ is the linear magnetoelectric coupling tensor, $\beta_{ijk}, \gamma_{ijk}$ ... are the nonlinear magnetoelectric coefficients. Hence, by differential calculus, one obtains [1]:

$$P_i(E, H) = -\frac{\partial F}{\partial E_i} = P_i' + e_{ij} E_j + e_{ij} H_j + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_j H_k + \gamma_{ijk} H_j E_k + ...$$

$$M_i(E, H) = -\frac{\partial F}{\partial H_i} = M_i' + \mu_{ij} H_j + \alpha_{ij} E_j + \beta_{ijk} H_j E_k + \gamma_{ijk} E_j H_k + ...$$

(2)

In multiferroics, the expressions is not so rigorous because $\varepsilon_{ij}(T)$ and $\mu_{ij}(T)$ display field hysteresis. Generally, ferroics are better parameterized in terms of resultant rather than applied fields. In practice, terms of superior order can be neglected, the calculation of $\alpha$, $\beta$ and $\gamma$ coefficients being sufficient for the permittivity and permeability tensors determination.

The following valuable inequality is valuable, which indicates that a large magnetoelectric effect is associated with great values for the permittivity, respectively permeability of the constituents included in the structure [10]:

$$\alpha_{ij}^2 \leq e_{ij} \mu_{ij}$$

(3)

Consequently, materials where chosen as a double perovskite (electric permittivity $\varepsilon_r \sim 134$) which is magnetoelectric and hexaferrites of M-type, with large magnetic permeabilities ($\mu_r \sim 700-800$). Considering the effective values for the susceptibilities, the magnetoelectric voltage coefficient for the polycrystalline samples can be written as:

$$\alpha_{ME} = \frac{dE}{dH}$$

(4)

and will be calculated using the data given the HFSS program for our nanocomposite model.
3. Core-shell magnetoelectrics

The magnetoelectric configurations of nanoparticles which we have considered in our study can be described as nanospherical configurations versus nanotubes: spherical core-shell structures, with magnetostrictive core and piezoelectric shell, respectively cylindrical core-shell structures with magnetostrictive rod and piezoelectric cylindrical coating. The external piezoelectric shell is represented by the Bi$_2$NiMnO$_6$ double perovskite and the magnetic inner core is a AFe$_{12}$O$_{19}$ M-type hexaferrites, with A an alkali earth metal: Ca, Sr, Ba.

Characteristics of the crystalline lattice for each phase can be summarized: for the Bi$_2$NiMnO$_6$ perovskite: lattice parameters (monoclinic, space group C121): $a = 9.4646(4)$ Å, $b = 5.4230(2)$ Å, $c = 9.5431(4)$ Å, and $\beta = 107.823(2)^\circ$ [9], [11]; for M hexaferrites: lattice parameters (space group P6$_3$mc): BaFe$_{12}$O$_{19}$: $a = 5.892$ Å, $c = 23.183$ Å; SrFe$_{12}$O$_{19}$ $a = 5.8808$ Å, $c = 23.2018$ Å; CaFe$_{12}$O$_{19}$: $a = 5.8303$ Å, $c = 22.1652$ Å. The M hexaferrites have a RSR*S* crystallographic build up, with $2M$ molecules per unit cell (figure 1). The structure is hexagonal, represented by a backbone of oxygen anions, the interstices of the close-packed oxygen lattice being occupied by metallic cations, magnetic and nonmagnetic. The cations usually have either four- or six-fold coordination and form tetrahedral, octahedral or trigonal sublattices [12].

The ionic radii of the atomic species included in the considered phases are: cations: Bi$^{3+}$ = 1.17 Å, Ni$^{2+}$ = 0.83 Å, Mn$^{2+}$ = 0.81 Å, Mn$^{3+}$ = 0.72 Å, Fe$^{2+}$ = 0.75 Å, Fe$^{3+}$ = 0.69 Å, Ba$^{2+}$ = 1.49 Å, Ca$^{2+}$ = 1.14 Å, Sr$^{2+}$ = 1.32 Å; anion: O$_2^-$ = 1.26 Å [8].

**Figure 1**. a) Structure of the monoclinic Bi$_2$NiMnO$_6$ double perovskite (after Langenberg [11]); b) the RSR*S* crystallographic build up of the M hexaferrite (source Mariño-Castellanos [12]).

The core-shell nanocomposites analysed with our simulation model (figure 2) have an external sphere diameter / cylinder length of 80 – 100 nm to 360 nm, an inner sphere / rod diameter of 20 to 60 nm. Samples are polycrystalline and the intrinsic dimensions depend also on the size of the pores of the membrane. We have estimated that dimensions and relative positions of the nanoconstituents can be controlled in a percent of ± 20 %, based on the data reported in literature. Two stages are indicated in the manufacturing process of the core-shell configurations: synthesizing of the ferrite / ferroelectric nanoparticles and covering the ferrite particle core (sphere or rod) with ferroelectric particle shell. Chemical methods are prefered, not sintering at high temperatures due to the advantages offered by the chemical low temperature processes [3]. Different methods were reported, such as: the sol-gel process followed by coaxial electrospinning, the template-assisted liquid phase deposition (LPD) method [2], [4].

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Properties control can be achieved by: modifying the chemical composition of the constituents (the ferrite core in our case), or by varying the ferrite / perovskite ratio by changing the wall thickness of the shell or the core diameter. The shape factor was modified inside the limits predicted by the theory, in order to obtain materials with tunable properties and reproducible characteristics. New possibilities of tuning and control were investigated, using the simulation model of the core-shell ferrite – ferroelectric structures.

At simulation we have to consider the peculiarities offered by the core-shell geometry such as high surface contact between the components and separation of the magnetic particle groups encapsulated in the perovskite shell. The processes at particle interfaces are dependent on the stain generated at interfaces by the magnetostrictive phases, on the degree of coupling with the electric phase and on the interfaces properties: characteristics of the interfaces at the atomic scale, presence of the voids, the curvature of the surface, the intrinsic contact area, etc. [7, 10, 11].

4. Results for the magnetoelectric coefficients

A simulational study was performed in order to determine the influence of the constituents shape on the properties control process of the nanocomposites, realized by an applied magnetic field. Core-shell nanospheres versus nanotubes structures were considered for comparison. Different hexaferrites were taken into account by changing the A alkali earth metal in the AFe$_{12}$O$_{19}$ combination.

Samples (4 x 0.8 x 12 mm$^3$) were simulated inside a rectangular waveguide WR-51 (R180 IEC Standard, K band), excited on TE$_{10}$, 1mW incident power at the input / output ports (figure 3.). The S parameters were determined for each nanoparticle configuration. The testing field has the frequency in the domain of 16 – 28 GHz, above the ferrite resonances. An 100 – 270 Oe external magnetic field was applied parallel with the propagation direction inside the waveguide, for controlling the electromagnetic properties of the nanoparticle samples (magnetic field influences the piezoelectric
deformation of the nanocomposite). The response of the core-shell nanoparticle samples is function of the particles geometrical configuration, coordinated by the strength of the magnetoelectric effect inside the material [6, 7, 9].

The components of the magnetoelectric coefficient tensor have been calculated using a physical algorithm based on the near-filed values in the particles vicinity, generated by the HFSS program. The magnetoelectric voltage coefficient \((dE/dH)\), of tens of mV/cm·Oe for the considered nanocomposites) has also been computed for each particles configuration. Results for the magnetoelectric voltage coefficient \((dE/dH)\) were represented in figures 4 – 7.

**Figure 4.** Evolution of the magnetoelectric voltage coefficient \((dE/dH)\) in function of the applied magnetic field \(H_0\), in the composites with nanospheres, respectively nanotubes.

![Figure 4](image)

The \(\alpha_{ME}\) coefficient increases with the applied magnetic field \(H_0\), due to the intensifying of the magnetoelectric effect inside the material samples. Magnetostriiction in the magnetic phase is increased, the coupled piezoelectric phase generating a higher polarization. The increasing of the ME effect is almost linear in the case of the nanosphere composites and evolves parabolic at nanotubes. Due to the higher agglomeration of magnetic particles in the rod core inside the cylinder, higher field are necessary to overlap the magnetic interactions between particles and to favour magnetostriiction.

The magnetoelectric coefficient decreases slowly with frequency over the ferrimagnetic resonance, as the theory predicts [1], [3], [10], the decreasing being more arched at nanospheres having more accentuate individuality concerning the interactions between constituent particles.

The influence of the shape factor on the magnetoelectric effect inside the material samples was illustrated on graphs in figures 6–7. For an applied magnetic field of 240 kOe, considered optimum for the compromise polarization / energy consumed, the testing frequency was of 16 GHz. The average dimensions of the core-shell particles were varied in the range of 20 to 60 nm for the magnetostrictive inner sphere or rod diameter, respectively of 80 – 200 nm / 80 - 360 nm for the external piezoelectric sphere diameter / cylinder length.

![Figure 5](image)

**Figure 5.** Evolution of the magnetoelectric coefficient in function of frequency, for an applied magnetic field \(H_0=240\) Oe.
Magnetization is directly dependent on the molar fraction of the ferrite phase (controlled by the average diameter of the magnetic core, $d_{\text{int}}$), as so as the electric permittivity increases when the ferroelectric ratios increases because of the enhanced influence of the ferroelectric regions which surround the ferrimagnetic regions [4]. Even if the magnetic permeability of the ferrite increases with the applied $H_0$, the reduction in the thickness of the shells results in a higher interaction between the magnetic cores [2], [4] the global ME effect being softening, even drastic at low values of $d_{\text{ext}} / l_{\text{ext}}$. The same effect of ME softening due to the core interactions appears also when the core dimensions increases over an optimum, which can be determined by simulation methods.

5. Conclusions

Core-shell nanocomposite structures of ferroelectric – ferromagnetic particles have been studied by simulation methods, in order to determine the influence of the shape factor on the strength of the magnetoelectric effect inside the polycrystalline material samples. Each composite configuration presents specific advantages in respect with the control process by the external magnetic field, considering that the effect of the resulting dipolar field generation is strongly anisotropic. Simulations are coming to help us to decide on the proper nanoparticles shape and the optimal values for the applied fields necessary to obtain the desired magnetoelectric coefficient in certain conditions.

In the first instance, one remarks that the close-packed structures like core-shell configurations ensures a high degree of control with low energy consumption (the $H_0$ polarizing fields are consistently below 1 kOe).

Nanotubes are more easy to be controlled in higher polarization fields, while nanospheres respond almost linear to the magnetic control field. The magnetoelectric coefficient decreases slowly with frequency over the ferrimagnetic resonance, more flexured at nanospheres.

Variation of the geometrical dimensions of the components in the nanocomposite is a good solution to control the magnetoelectric properties of the nanotubes, the dimension influence being higher in their case. The nanospheres response at dimension modification is not so accentuate, but more modulated. The average diameter of the magnetic core controls the magnetization, as so as the ferroelectric ratios influence the electric permittivity, but by increasing the core dimensions over an optimum or by reducing the thickness of the shells, the global ME effect is soften.

Simulation methods impose themselves like powerful tools for analysing the nanomaterial properties at nanoscale, the methods being non-destructive. The results indicate us the proper nanoparticles shape factor and the optimal intensity of the applied fields in order to obtain the desired values of the ME coefficient for a specific material sample.
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