Field control of multiferroic spherical core-shell nanocomposites with applications in microwave range

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Abstract. Multiferroic spherical nanoparticle configurations consisting of magnetostrictive core encapsulated in piezoelectric shell have been studied. The particles were simulated in a test configuration with help of the HFSS 13.0 (by Ansoft). An external magnetic field was applied, which determines the apparition of dipolar electric fields of tens of milivolts around nanoparticle structures, used for tuning and control of different microstructures, at molecular level and in spintronics. The nanoparticle compounds are: an $A_2BB'O_6$ double perovskite with large piezoelectric coefficients and a $MeFe_2O_4$ spinel or a $AFe_{12}O_{19}$ M-type hexagonal ferrite with large magnetostriiction, resulting in nanoparticle configurations with large magnetoelectric (ME) effect. The strength of the ME effect is also increased by the effect of the closed-packed shape of the spherical core-shell configuration. Different magnetic phases (spinel versus hexaferrite) were considered, in order to determine their influence in the interaction process with the applied magnetic field. The diameter of the piezoelectric shell did not exceeded 300 nm, starting from about 50 nm. The components of the magnetoelectric coefficient tensor and the effective electric and magnetic susceptibilities have been determined by simulation in microwave range (2 – 8 GHz for spinel compounds, respectively 12 – 28 GHz for hexaferrite compounds), for different magnetic fields applied for control (0 – 400 Oe), fields depending on particles size. The tensor components depend on the physical properties of the constituents and also on the constituents geometry and relative position. Nanoparticle configurations geometry and the applied $H_0$ field were modified in order to obtain a convenient variation and control of the compound susceptibilities. Graphs are available for choosing the optimal configuration and parameter values for a specific application.

1. Introduction
Two or more ferroic phases characterizing the same structure determine the multiferroics category of materials and composites, with multiple applications in practice. Among these, magnetoelectric materials contain ferroelectric and ferromagnetic order components, in a nanocomposite structure. Example of such structures can be: core-shell nanoparticles, nanopillars, and nanowires (spherical or cylindrical ferromagnetic core with ferroelectric shell), composite spheres of piezoelectric ceramics or piezopolymers with embedded magnetic nanoparticles, multiferroic nanocomposite films with alternate ferromagnetic / ferroelectric layers, etc.
Magnetoelectric materials are used for applications like magnetic field sensors, magnetic data storage, ferromagnetic resonance devices, in magnetic-field-tunable microwave and millimeter wave devices, spintronic devices, where the electric field can control the magnetic effects and also the electric polarizability can be varied with help of an applied magnetic field.

Magnetoelectric composites have better properties if there are synthesized like composed phases, not single phases. The material components must have large magnetic and electric susceptibilities in order to determine a structure with large magnetoelectric coupling [1, 2]. Multilayered structures or core-shell configurations of multiple components present a large magnetoelectric effect due to the magnetostrictive and piezoelectric effects at phase boundaries, mediated by strain. In a magnetic filed, the magnetic phase suffers magnetostriction and the resulted strain is applied to the coupled electric phase, which modifies its electric polarization. Following the idea, the applied fields are used for controlling the structure properties, which can be modulated also by changing the components nature and their geometrical configuration.

2. Material structure

2.1. Core-shell configurations

Nanospheres with core-shell configurations were considered in this paper, presenting large magnetoelectric effect due to a proper choosing of the microscopic constituents. The electric phase consists of the piezoelectric shell, which was chosen like the Bi$_2$NiMnO$_6$ double perovskite (A$_2$BB’O$_6$), while the magnetic phase (ferrite core) is a MeFe$_2$O$_4$ spinel (Me = Mn, Ni) or a XFe$_{12}$O$_{19}$ M-type hexaferrite (X = alkali earth metal: Ba, Ca, Sr). The core-shell composites with spinel versus hexaferrite were compared in order to determine the magnetic phase influence on the interaction process with the applied magnetic field and the material parameters modifications.

![Figure 1](image-url). Lattice structure of the electric, respectively magnetic phases:

a) Bi$_2$NiMnO$_6$ double perovskite (source: Zhao [10]); b) MeFe$_2$O$_4$ spinel (source: Ionic Crystals [8]); c) XFe$_{12}$O$_{19}$ M-type hexaferrite (source: Wang, 2014).
In the Bi$_2$NiMnO$_6$ double perovskite (monoclinic, space group C121, figure 1.a)), the Bi$^{3+}$ ions are located in the A sites and magnetic Ni$^{2+}$ and Mn$^{4+}$ ions are placed randomly in the B sites (in the three crystallographic sites (M(1), M(2), and M(3), with multiplicities of 2, 4, and 2, respectively) [11]. We have a monoclinic unit cell (space group C2), with \(a = 9.4646(4) \text{ Å} \), \(b = 5.4230(2) \text{ Å} \), \(c = 9.5431(4) \text{ Å} \), and \(\beta = 107.823(2)^\circ\). The monoclinic unit cells are superimposed. The perovskite itself is a multiferroic due to the combination between B and B’ magnetic ions, which give rise to a ferromagnetic coupling.

The magnetic phases: in the spinels (space group \(Fd3m\)) the lattice of O$^{2-}$ ions forms tetrahedral and octahedral local symmetry that are referred to as A and B sites, respectively (figure 1.b)). The MnFe$_2$O$_4$ spinel has \(a = 8.4764 \text{ Å} \), respectively the NiFe$_2$O$_4$ spinel has \(a = 8.3378 \text{ Å} \) [5]. For hexaferrites (figure 1.c), space group \(P6_3mc\), the lattice parameters are: BaFe$_{12}$O$_{19}$: \(a = 5.892 \text{ Å}, c = 23.183 \text{ Å} \); SrFe$_{12}$O$_{19}$: \(a = 5.8808 \text{ Å}, c = 23.2018 \text{ Å}; \) CaFe$_{12}$O$_{19}$: \(a = 5.8303 \text{ Å}, c = 22.1652 \text{ Å}. \) The ionic radii of the atomic species included in the considered phases are: cations: Bi$^{3+} = 1.17 \text{ Å}$, Ni$^{2+} = 0.83 \text{ Å}$, Mn$^{2+} = 0.81 \text{ Å}$, Mn$^{3+} = 0.72 \text{ Å}$, Fe$^{2+} = 0.75 \text{ Å}$, Fe$^{3+} = 0.69 \text{ Å}$, Ba$^{2+} = 1.49 \text{ Å}$, Ca$^{2+} = 1.14 \text{ Å}$, Sr$^{2+} = 1.32 \text{ Å};$ anion: O$^{2-} = 1.26 \text{ Å} $ [3].

The core-shell nanoparticle configurations were reconstructed using the 3D structural simulation program HFSS 13.0 (by Ansoft) [10], [12], based on the information given in literature. Structures of this type were obtained by different methods, in two steps: synthesis of the core magnetic nanoparticles and covering them with a piezoelectric shell. Examples of different combinations reported in literature: (BaTiO$_3$+NiFe$_2$O$_4$) obtained by magnetic-field-assisted assembly [1]; (BaTiO$_3$+CoFe$_2$O$_4$) prepared using a combination of solution processing and high temperature calcinations [7]; (BaTiO$_3$+CoFe$_2$O$_4$): ferrite nanoparticles prepared through a polyacrylamide gel method, and then coating with ferroelectric using the same gel route [3]; similar - synthesized by combining co-precipitation and organosol methods [6]. Characteristic of the phases are to be observed from there references, in order to define a proper simulational model for the structures. The core-shell configuration has an important role to play in formation of a defined interface between the magnetostrictive and piezoelectric phases, the strain caused by the core and/or shell giving rise to the giant ME coupling. The constituent nanoparticles are polycrystalline (with a random orientation of the particles inside the piezoelectric shell) of ca. 25 - 80 nm for the core magnetic particles, respectively of 20 - 30 nm for the piezoelectric particles in the shell. Diameter of the piezoelectric shell was considered in the range of 60 - 300 nm (Figure 2) and the interdiffusion region of c few nanometers

### 2.2. Theoretical considerations

For the composite structures, the magnetoelectric coefficient tensor \( \alpha \) is given by the formula [2], [9]:

\[
D_i = \sum_{j=1}^{3} \varepsilon_{ij} E_j + \sum_{j=1}^{6} \varepsilon_{ij} S_{wj} + \sum_{j=1}^{3} \alpha_{ij} H_j \quad i = 1,3
\]
where $D$ = the electric flux density (the response) in multiferroic composite; $E_j$ represents the components of the applied electric field, $S_j$ are the components of the external mechanical stress, $H_j$ are the components of the applied magnetic field vector; $e_{ij}$ are the permittivity tensor components, $e_{ij}$ are the piezoelectric coefficients and $\alpha_{ij}$ are the components of the magnetoelectric tensor.

The electromagnetic properties of the electric, respectively magnetic phase depend on the electric / magnetic dipole configuration and the lattice structure. An important role is played by the spin-lattice coupling and distinct interactions between spin and dipole [5]. We had to consider that the domain structure is dynamic under the applied fields, meaning that the domain wall thickness and domain width are changeable. For the double perovskite, which is multiferroic, the ferroelectric domain walls present a net magnetization even if the domains are paramagnetic.

The electric, respectively magnetic susceptibilities have been determined using the data given by the HFSS program for the fields inside and outside the material samples:

$$\chi_e(E,H) = \frac{\partial P}{\partial E}, \quad \chi_m(E,H) = \frac{\partial M}{\partial H}. \quad (2)$$

### 3. Simulation determinations

In the test configuration, the core-shell structures of nanoparticles of different nature were exposed to a magnetic field in the domain 0 – 400 Oe. As a result, a dipolar electric field of tens of milivolts is generated around each core-shell structure, which can be used in practice for tuning and control of different microstructures [4], [10].

![Sample slab inside the rectangular waveguide](image)

**Figure 3.** Sample slab inside the rectangular waveguide. The polarization magnetic field $H_0$ is parallel with the Oz propagation direction.

Samples with dimensions of $4 \times 0.8 \times 12 \text{ mm}^3$ were placed inside the WR-187 rectangular waveguide ($47.5488 \times 22.1488 \text{ mm}^3$), excited by TE$_{10}$ mode (figure3.). A static field $H_0$ for polarization was applied on Oz propagation direction, parallel with the long side of the sample. 1mW incident power was applied in the simulation model at each port for determining the $S$ parameters at propagation through the waveguide loaded with sample. The electromagnetic coefficients, electric effective permittivity, respectively magnetic effective permeability of the core-shell polycrystalline samples were calculated from a two-port measurement, using the transmission and reflection coefficients measured with the sample inside in the waveguide. Determinations were made at frequencies above the ferromagnetic resonance of the material samples.

Different magnetic phases (spinel versus hexaferrite) were considered, in order to determine their influence in the interaction process with the applied magnetic field and the capabilities of the modulation of the electric field generated by the nanoparticles, used in applications.

Simulations were performed in microwave range (2 – 8 GHz for spinel compounds, respectively 12 – 28 GHz for hexaferrite compounds). The $H_0$ induced variations in the electric, respectively magnetic susceptibilities are illustrated in the graphs below (figures 4 - 5).
Figure 4. Real and imaginary parts of the electric / magnetic effective susceptibility, $\chi_e$, $\chi_m$, for the considered core-shell nanocomposites with spinels ($\text{Bi}_2\text{NiMnO}_6 + \text{NiFe}_2\text{O}_4$; $\text{MnFe}_2\text{O}_4$). The curve with optimum points is indicated on graphs.

The curve with the optimum points was illustrated on graphs (the dash curve), each point indicating the value of the applied magnetic field, at a given frequency, necessary to obtain the maximum of the electric polarization corresponding to each nanoparticle configuration. The line of the optimum points can be represented on the graphs of all the susceptibility components, in order to obtain a complete characterization of the material in an optimum point.

The susceptibility values depend on the physical properties of the constituents (the piezoelectric coefficients of the ferroelectric, respectively the piezomagnetic coefficients of the ferrimagnetic phase), and also depend on the constituents geometry and relative position. All these quantities can be fine modified in the structural simulation model when the simulations are performed.

The values of the effective electric relative permitivities, respectively magnetic permeabilities have been calculated for the spinel nanocomposites, respectively for the nanocomposites with hexaferrites. Values in the range of 145 – 152 have been obtained for the composites permittivity, higher values for hexaferrites. For the composites permeability, values of about 592-594 were obtained for structures with $\text{NiFe}_2\text{O}_4$, respectively of about 680-686 for structures with $\text{MnFe}_2\text{O}_4$. For composites with hexaferrites, $\mu_{\text{r,eff}}$ was calculated of around 743-745 for structures with $\text{CaFe}_{12}\text{O}_{19}$, of around 736-738 for structures with $\text{SrFe}_{12}\text{O}_{19}$, respectively of around 733-734 for composites with $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite.
4. Conclusions
Core-shell nanocomposites with ferrite – ferroelectric constituents and presenting strong magnetoelectric effect due to close-packed configuration and strain transmission through the certain boundaries have been analyzed in this paper. Magnetic field intensity was modified in order to obtain a convenient variation and control of the electric and magnetic susceptibilities of the nanocomposites. For all compounds, the magnetic susceptibility increases with the applied $H_0$. For the composites with spinels, the real part of the electric susceptibility, related to the stored energy within the medium, presents a flexional evolution with the applied field. The curvature modification is a result of the internal processes at sample level (the stain generated by magnetostriction reaches a threshold value and over it the induced electric polarization evolves after a different law with the applied field).

The imaginary parts of the susceptibilities, related to the dissipation of energy within the medium, increases with the applied field and also with frequency. Magnetic losses increases faster, being relative low up to the values of the applied field of about 200 Oe, due to the influence of the resonant energy absorptions which are present over these vales of the field.

For the composites with hexaferrites, curves of evolution of the susceptibility components versus the applied magnetic field are more flat and susceptibilities preset superior values. More magnetic iron ions in the lattice confer a stability of the composite response and lower variations under the applied magnetic fields. Magnetic losses evolve with $H_0$ not so abruptly, losses being consistent even at lower
values of the applied field (this fact indicates energy consumption for magnetic processes at sample level).

Curves with optimum points are illustrated on graphs, in order to recommend the set of punctual parameters which have to be chosen for obtaining the maximum of the electric polarization induced by the applied magnetic field. The simulation method is a non-destructive analysis method, with solutions for choosing the field parameters and geometrical / physical sample configuration.

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