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STUDY OF THE DIFFUSION CONTROLLED PROPERTIES IN THE FERRITE - FERROELECTRIC NANOCOMPOSITES

Daniela IONESCU[1], Daniel MĂTĂSARU[2], Viviana RADU[3]

Ferromagnetic - ferroelectric systems (hexagonal ferrite - ferroelectric perovskite) were considered in this paper, which can be synthesized like high permeability and high permittivity nanocomposites. The microstructure and properties depend on the thickness of diffusion layer at nanograins boundaries and of the element distribution in this layer and can be reproduced by simulation. A study of the diffusion properties in function of substitution ion's properties (radius, charge, electric and magnetic moment) was performed. Electromagnetic parameters of the nanocompozite were illustrated on parametrical graphs in microwave range. The control parameters characterize the diffusion layer. A ferromagnetic - ferroelectric system tunability ranging from 7 to 16% was achieved, depending upon the mechanism of diffusion.

Key words: hexaferrite, diffusion layer, nanograins, structural simulation, permittivity, permeability, control parameters.

1. Introduction

System-on-a-Package technology with digital, RF, and optical system integration on a single package and also the MEMS systems require materials with special properties, like the composites with both inductance and capacitance integrated in one element. The new synthesized ferrite-ferroelectric composite ceramics present high magnetic permeability and also high electric permittivity. The spinel ferrites are used as magnetic phase, for their compatibility with the LTCC manufacturing process. For higher frequency applications, the hexagonal ferrites are recommended, such as the barium ferrites: *M*, *Y* or *Z* type, with different substitution ions in a proper volume ratio to control their properties. Multiple applications can be mentioned: anti electromagnetic interference (EMI) filters, multilayer chip LC filter [1], [11], [13], etc.

The nanocomposites are prepared in practice by sintering at 1200- 1220 ^{0}C for circa 3 h after mixing and milling [4], [5]. The mixture is obtained by ions diffusion between the ferrite and ferroelectric grains during the sintering process at high temperature [4], [2]. The microstructure and properties of the composite

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[1] Assistant Prof., Depart. of Telecommunications, "Gh. Asachi" Technical University of Iasi, Romania, e-mail: danaity@yahoo.com

[2] Assist., Depart. of Telecomm., "Gh. Asachi" Technical University of Iasi, Romania

[3] PhD Student, Department of Physics, "Al. I. Cuza" University of Iasi, Romania

depend on the thickness of diffusion layer and of the element distribution in this layer and can be reproduced by simulation. The diffusion coefficient is function of the substitution ions properties (radius, charge, electric and magnetic moment).

The composite ceramics with powder mixture have much better cofiring behavior than the multilayered ceramics, due to the large amount of grain boundaries to dissipate stress. Diffusion is a controlled process, but we have also to consider that the results can affected in practice by the undesirable cofiring defects such as delaminations, cracks and cambers, due to the mismatching of the sintering kinetics and different thermodynamic parameters of the ferrite and ferroelectric. Secondary effects can also accompany the significant element diffusion at the nanograins interface, such as the formation of new phases which affect the properties of co-fired composite ceramics and grain growth near the interface. During the cofiring, the crystal morphology and orientation can be changed due to the differences of densification.

Hexagonal ferrites have a lower sintering temperature of around 1100 ^{0}C, which determines a good cofiring behavior for the composites (fewer defects) and a high density close to the theoretical value, in association with a ferroelectric with similar sintering temperature and densification behavior [14], [2].

2. Characteristics of the Method

2.1. Simulational model

In the two-phase nanocomposite ((1-y) ferrite / y ferroelectric), the magnetic phase is represented by one of the following Z-type hexaferrite:

- $Ba_3Co_2Fe_{24}O_{41}$ (or Co_2Z) - $\mu_{eff} \approx 15$ and $\varepsilon_{eff} \approx 17.8$ at 1 GHz [1], varying with frequency up to 20% in microwave range. Grain size is of 190 - 400 nm.
- $Ba_3Co_{2(1-b)}Cu_{2b}Fe_{24}O_{41}$ (Cu-modified Co_2Z, $b = 0 - 0.25$) - $\mu_{eff} \approx 13.2$ and $\varepsilon_{eff} \approx 20.7$ at 1 GHz [1], [3], presenting a slow variation with the Cu content; the grain size is of 100 - 280 nm.
- $Ba_3Co_{2(0.8-b)}Cu_{0.40}Zn_{2b}Fe_{24}O_{41}$ (Cu-modified Co_2Z with Zn incorporated, $b = 0 - 0.25$) - $\mu_{eff} \approx 11.8$ and $\varepsilon_{eff} \approx 22$ at 1 GHz [1], depending on the substitution ions properties and varying slowly with frequency. Grain size is of 60 - 240 nm.

The magnetic permeability of the magnetic phase can be modified considering that the magnetism of polycrystalline ferrites is a consequence of spin rotation and domain walls motion [10,15]. The control parameters are: the grain size, densification, an applied static field H_0 (~ 5-10 kOe), internal stress, etc.

The ferroelectric phase is represented by the $Ba_xSr_{1-x}TiO_3$ ferroelectric perovskite (BSTO, $x = 0.75 – 1$). The BSTO has $\varepsilon_{eff} \approx 2620 - 3740$ at 1 GHz (does not exhibit significant frequency dependence in microwave range), which is function on substituting ions content in the perovskite. The average grain size is of 18 - 48 nm in pure phase. The tunability of the permittivity [1], [6], [9] can be achieved by changing the bias voltage (~ 2-20 kV/cm) or considering the changes in microstructure including the grain size, texture misalignment, interfacial amorphous layer, surface roughness and deterioration of the Bragg reflector layers

Samples are polycrystalline, the morphology of the grains being a bit different than that of the pure phases (the grains are growing randomly near the interface up to 20 % [1]). In the same time, different authors have reported that the average size of ferroelectric or ferrite grains decreases with the rise of corresponding phase amount [4]. The crystalline structure of the nanograins [1], [12] was reproduced by simulation or by image analysis [16]: for the *Z*-type ferrites we have a MYMY crystallographic build up, space group: $P6_3/mmc$, with a no. of molecules /unit cell of 2*Me*Z, while the ferroelectric perovskite has a tetrahedral crystal structure, space group *P4mm*.

The simulational model was conceived to illustrate the high permeability of the ferrite, induced by the high crystallographic uniaxial anisotropy and the high permittivity of the ferroelectric perovskite. We have applied the equivalent dipole representation of the composite, for which the effective permeability and permittivity are function of the intrinsic dipole moments per volume unit and volume fraction of the constituents. The effective electromagnetic parameters are controlled by the diffusion layer, whose properties depend on the substitution ions which penetrate between the material phases at the grain boundaries.

The ionic species which can be found in the diffusion layer are bold written in Table 1, which gives the ions radius, charge and magnetic moment in the nanocomposite.

Table 1

Ionic properties (radius, charge and magnetic moment) of different atomic species included in the ferrite-ferroelectric nanocomposite.

Ion	Ba^{2+}	**Ti^{4+}**	**Fe^{3+}**	**Fe^{2+}**	**Co^{2+}**	**Zn^{2+}**	**Cu^{2+}**	**Mn^{3+}**	**Mg^{2+}**	Sr^{2+}	O^{2-}
Ionic radius *r* [nm]	0.135	0.074	0.076	0.064	0.074	0.074	0.072	0.066	0.086	0.158	0.126
Magnetic moment ($\mu_{spin\text{-}only}/\mu_B$)	0	0	5.92	4.90	3.88	0	1.73	4.90	0	0	0

Ions which can substitute Co in the barium hexaferrite (Cu, Zn, Mg, Mn) diffuse into the perovskite lattice. The Co ions also diffuse and even the Fe^{3+} ions diffuse from the ferrite into the ferroelectric [1], [2]. The Ti ions diffuse into the ferrite, the Ba or Sr ion do not diffuse due to the large radius. At the simulation we have consider that each ion dynamic of diffusion depend on ion's properties, of the properties of the receiving lattice and spatial distribution of the other diffusant species. The considered ion species distribution in the diffusion layer is given in Table 2.

Table 2

Distribution of the diffusive ion species in the diffusion layer.

Ion	**Ti^{4+}**	**Fe^{3+}**	**Fe^{2+}**	**Co^{2+}**	**Zn^{2+}**	**Cu^{2+}**	**Mn^{3+}**	**Mg^{2+}**
Volume ratio [%]	2	14	5	18	7	5	13	4

If the sintering temperatures of the compounds are similar, one can consider that the ferrite / ferroelectric grains distribute homogeneously. Due to the slight modification of the grain size with the corresponding phase amount, an equilibrate composition is recommended ($y \sim 0.4 - 0.7$). In practice, y can vary up to 0.9 without considerable grain size modification due to the fact that internal stress and lattice distortion during the cofiring process favour a compact-stacked grains structure and obstruct the grain size modification.

2.2 Operational equations

The ferromagnetic - ferroelectric diffusion can be generally described by the Fick's first law, where the diffusive flux is proportional to the concentration gradient (spatial derivative):

$$J = -D \cdot \nabla \phi, \tag{1}$$

with J [mol/m^2·s] is the diffusion flux or the amount of diffused substance per unit area per unit time; D [m^2/s] is the diffusion coefficient or diffusivity and Φ [mol/m^3] represent the concentration.

In polycrystalline materials we have to use the effective diffusion coefficient, which is a combination of lattice, and grain boundary diffusion coefficients. The effective diffusion coefficient of each diffusant can be modeled using Hart's equation [7]:

$$D^{eff} = f \cdot D_{gb} + (1 - f) \cdot D_l, \tag{2}$$

where D^{eff} = effective diffusion coefficient; D_{gb} = grain boundary diffusion coefficient; D_l = lattice diffusion coefficient; f =(δ / $\overline{g}$) is the area fraction of grain boundary, δ is the grain boundary width, and $\overline{g}$ the mean linear intercept grain size.

Concerning the temperature dependence of the diffusion coefficients, diffusion along both the grain boundary and in the lattice can be modeled with an Arrhenius equation, the diffusion being more active when temperature is lower.

The perovskite-type material with crystalline nanograins is non-linear and electric anisotropic. In the same time, the ferrite is also a non-linear material and magnetic anisotropic. The $\overline{\overline{\chi_e}}(E)$, respectively $\overline{\overline{\chi_m}}$ susceptibility tensors depend on crystalline phase structure, on the structure of nanograins and of the diffusion layer. Our physical algorithm for determination of the electromagnetic parameters of the nanocomposite is based on calculation of the energy density variation when the testing field propagates through the material sample [8]. The Poynting's theorem in integral form was used:

$$\frac{\partial}{\partial t} w \cdot dV + \oint_{\partial V} \boldsymbol{S}_{poynting} \cdot d\boldsymbol{A} = -\int_{V} \boldsymbol{J} \cdot \boldsymbol{E} \cdot dV \tag{3}$$

where $\boldsymbol{S}_{Poynting} = \boldsymbol{E} \times \boldsymbol{H}$ = Poynting vector, w represents the energy density, with electric respectively magnetic parts: $w = w_e + w_m$; $\boldsymbol{J}$ is the current density and ∂V is the surface which encloses the sample volume V.

For a finite number of the sinusoidal field periods, the dw_e, respectively dw_m variations are linked by the electric susceptibility tensor components:

$$dw_e = \boldsymbol{E} \cdot d\boldsymbol{P} = \boldsymbol{E} \cdot d(\varepsilon_0 \cdot \overline{\overline{\chi_e}} \cdot \boldsymbol{E}) = \varepsilon_0 \cdot \left(\boldsymbol{E} \cdot \overline{\overline{\chi_e}} \cdot d\boldsymbol{E}\right) \tag{4}$$

$$dw_m = \boldsymbol{H} \cdot d\boldsymbol{M} = \boldsymbol{H} \cdot d(\overline{\overline{\chi_m}} \cdot \boldsymbol{H}) = \left(\boldsymbol{H} \cdot \overline{\overline{\chi_m}} \cdot d\boldsymbol{H}\right) \tag{5}$$

For the susceptibilities determinations, the dw_e, respectively dw_m variations were calculated using the data given by the HFSS program. By varying different structural or diffusion parameters, the evolutions of the nanocomposite permittivity and permeability were obtained, in the microwave range (20 GHz).

3. Results for the electromagnetic parameters

The Hart's equation predicts a linear increasing dependence of the effective diffusion coefficient on the grain boundary width δ and a decreasing of $(1/\overline{g})$ type with the grain size. The study of the diffusion properties in function of substitution ion's properties (radius, charge, electric and magnetic moment), which are also diffusive, was performed here by simulation method. The dynamic of the diffusion layer is a complex function of time and diffusive ions properties, consequently the dimensional parameters were mediated at interface level. In Figure 1 are illustrated the results for the $Ba_3Co_{1.2}Cu_{0.40}Zn_{0.4}Fe_{24}O_{41}$ / y $Ba_{0.9}Sr_{0.1}TiO_3$ composite, which contains a great number of ions in the diffusion layer. The control parameter were considered here the mean linear intercept grain size $\overline{g}$.

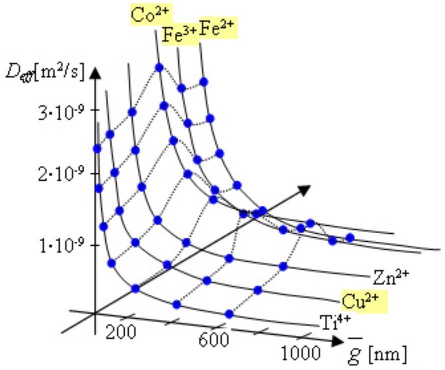

Fig. 1. Simulation results for the diffusion coefficient of the diffusive ion species in the (1-y) $Ba_3Co_{1.2}Cu_{0.40}Zn_{0.4}Fe_{24}O_{41}$ / y $Ba_{0.9}Sr_{0.1}TiO_3$ ferrite - ferroelectric nanocomposite versus the mean linear intercept grain size $\overline{g}$.

The diffusion layer properties influence the effective electromagnetic parameters of the nanocompozite. The energy variation method for the susceptibilities determination has given us the results presented in figures 2, respectively 3. The exciting field was considered in microwave range (20 GHz) where most of the applications of the ferrite - ferroelectric nanocomposite work.

Effective permittivity, respectively permeability of the nanocomposites with the three considered types of Z hexaferrites where represented on graphs for different concentration of phases. Electromagnetic parameters can be controlled by varying the $\overline{d}/\delta$ ratio, where $\overline{d}$ represent the average thickness of the diffusion layer at nanograin boundaries and δ is the grain boundary width. The effective permittivity ε_{eff} decreases with increasing of the diffusion layer thickness over a specific value denoted with $\overline{d}_{cr}$ which depend on the crystalline structure of the nanograins and do not depend on the concentration of phases. The effective permeability present a valley on graphs at $\overline{d}_{cr}$, the μ_{eff} increasing over this value but decreasing slightly for higher $\overline{d}/\delta$ ratio. Even if the $\overline{d}_{cr}$ value is imposed by the crystalline structure, in this case the modification of ferrite structure which imposes the μ_{eff} shifts the $\overline{d}_{cr}$ value of the three nanocomposites.

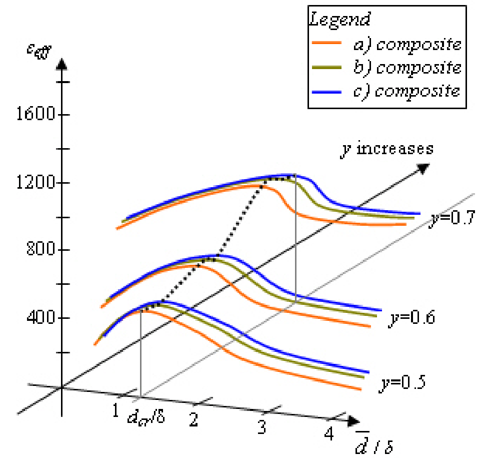

Fig. 2. Effective permittivity versus the $\bar{d}/\delta$ ratio, for *a)* (1-*y*) $Ba_3Co_2Fe_{24}O_{41}$ / *y* $Ba_{0.9}Sr_{0.1}TiO_3$; *b)* (1-*y*) $Ba_3Co_{1.6}Cu_{0.4}Fe_{24}O_{41}$ / *y* $Ba_{0.9}Sr_{0.1}TiO_3$ and *c)* (1-*y*) $Ba_3Co_{1.2}Cu_{0.40}Zn_{0.4}Fe_{24}O_{41}$ / *y* $Ba_{0.9}Sr_{0.1}TiO_3$ nanocomposites.

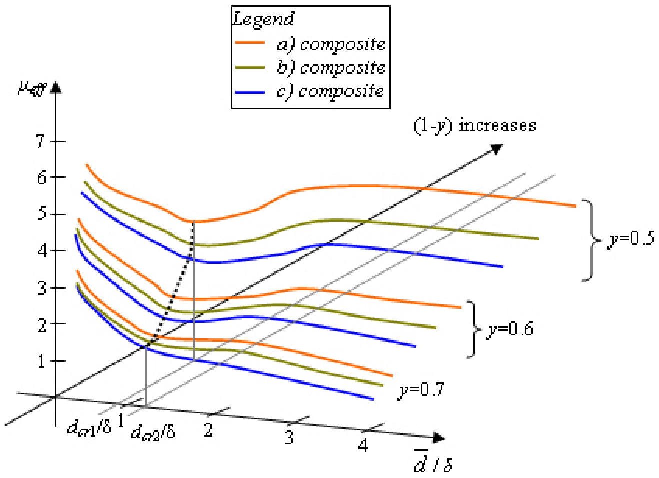

Fig. 3. Effective permeability versus the $\bar{d}/\delta$ ratio, for *a)* (1-*y*) $Ba_3Co_2Fe_{24}O_{41}$ / *y* $Ba_{0.9}Sr_{0.1}TiO_3$; *b)* (1-*y*) $Ba_3Co_{1.6}Cu_{0.4}Fe_{24}O_{41}$ / *y* $Ba_{0.9}Sr_{0.1}TiO_3$ and *c)* (1-*y*) $Ba_3Co_{1.2}Cu_{0.40}Zn_{0.4}Fe_{24}O_{41}$ / *y* $Ba_{0.9}Sr_{0.1}TiO_3$ nanocomposites.

The ferrite - ferroelectric composites are complex systems for which the electromagnetic parameters depend on a sum of factors, structural and external. Some of these factors can be used like control factors for the effective parameters values in the domain of interest for specific applications, like the thickness of the diffusion layer in our case. Other influences on the electromagnetic parameters are due to the material effects, like the magnetoelectric effect, which is present for the ferrite - ferroelectric composites but for the considered compounds is weak.

The cofiring process in practice has to be carefully monitored in order to offer reproducible results, which can be obtained also by simulation. The mechanical interaction between the two constituent phases has to be weak and the internal stress produced during the cofiring process has to be as low as possible, not to influence the magnetization.

4. Discussions and Conclusions

For the ferromagnetic - ferroelectric polycrystalline nanocomposites consisting of barium Z hexagonal ferrites and barium strontium titanate ferroelectric perovskite, the microstructure and properties depend on the diffusion dynamics at nanograins boundaries and can be reproduced by simulation.

The effective diffusion coefficient of each diffusant can be modeled using Hart's equation. The $\overline{\overline{\chi_e}}(E)$, respectively $\overline{\overline{\chi_m}}$ susceptibility tensors depend on crystalline phase structure, on the structure of nanograins and of the diffusion layer and were determined here by the energy variation method. A study of the diffusion properties in function of substitution ion's properties which diffuse was performed by simulation method. The electromagnetic parameters can be controlled by varying the ratio of the average thickness of the diffusion layer to the grain boundary width. The ε_{eff} presents a peak, respectively μ_{eff} a valley around a specific value $\bar{d}_{cr}$ which depends on the crystalline structure of the nanograins and do not depend on the concentration of phases.

A ferromagnetic - ferroelectric system tunability ranging from 7 to 16% was achieved, depending upon the mechanism of diffusion.

A good agreement with the results reported in literature was found for punctual results, in the case of the electromagnetic effective parameters of the considered nanocomposites. The reported results are only punctual and do not cover the whole range of parameter values considered by us. A relative error of ca. 2.8 % was estimated for the quantities determined by our simulation method.

For increasing the electromagnetic parameters tunability, practical methods can be considered like: alleviating the element diffusion, lowering the sintering temperature, etc.

Defects influence on the material parameters has to be reduced by avoiding the cofiring mismatch as much as possible. This can be solved by combining in the nanocomposite ceramics of the two constituent phases with similar sintering temperature.

We have also to consider that material resonances are present. This is an important fact for choosing the operating frequency subdomain for a specific application. The hexaferrites present a strong dielectric resonant peak, above a frequency of 100 MHz up to a few GHz (depending on the structure), caused by the dipole's vibration. Piezoelectric vibration is also present for the composite, in the MHz range. In the same time, hexaferrites are soft magnetic ferrites, consequently present a few more types of lower resonances, such as magnetic domain wall resonance and spin resonance. Their spectrum is very large, starting in the GHz region up to the THz region.

The effective permeability and permittivity present also frequency dispersion, as a phenomenon determined by the field - substance interaction and influenced by the microstructure. Fortunately the frequency dispersion of the ε_{eff}, respectively μ_{ef} do not exceed a few percents in their relative variation, if it is measured above the dielectric resonant peak for the considered materials and far from resonances.

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REFERENCES

[1] *E. Selezneva*, Magnetoelectric Composites Based on Hexagonal Ferrites, PhD Thesis, Universidade de Aveiro, 2008

[2] *Q.-W. Han, K. Li, S. Peng, Y. Wang, H. L.-W. Chan*, "Fabrication of the Cobalt Ferrite/Modified Sodium Bismuth Titanate 0-3 Multiferroic Composites *via* Diffusion-blocking", in Journal of Inorganic Materials, **vol. 26**, no. 5, 2011, pp. 486-490

[3] *Yang Bai, Fang Xu, Lijie Qiao, Ji Zhou, Longtu Li*, "The static and hyper-frequency magnetic properties of a ferromagnetic–ferroelectric composite", in Journal of Magnetism and Magnetic Materials, **vol. 321**, no. 3, February 2009, pp. 148–151

[4] *Feng Gao, Chang Song Zhang, Xiang Chun Liu, Chang Sheng Tian*, "The Interface and Grain Growth in Cofired Ferroelectric / Ferrite Multilayer Composites", in Materials Science Forum, **vols. 475 - 479**, 2005, pp. 1185-1188

[5] *C.-L. Miao, J. Zhou, Z.-X. Yue, L.-T. Li*, "Cofiring behavior of NiCuZn ferrite/PMN ferroelectrics di-layer composites", in Trans. Nonferrous Met. Soc. China, **vol. 15**, no. 2 (Sum. 65), Apr. 2005, pp. 225-228

[6] *Y.-A. Wang, Y.-B. Wang, W. Rao, J.-X. Gao, W.-L. Zhou, J. Yu*, "Electric and Magnetic Properties of the $(1-x)Ba_{0.6}Sr_{0.4}TiO_3$-$xCoFe_2O_4$ Multiferroic Composite Ceramics", Chin. Phys. Lett., **vol. 29**, no. 6, 2012, pp. 067701

[7] *T. P. Swiler, E. A. Holm*, "Diffusion in Polycrystalline Microstructures", 1996 MRS Fall Meeting & Exhibit, December 02-06, 1996, Boston, MA

[8] *D. Ionescu, I. B. Ciobanu*, "HF Study of the Electrical Permittivity for Some Perovskite-Like Systems from the Two Dimensional Perovskite Layer Family", in Romanian Journal of Physics, **vol. 54**, nos. 9-10, 2009, pp. 899- 909

[9] *A. Ianculescu*, "Asupra efectelor dimensionale privind conservarea feroelectricitatii in sisteme micro- si nanostructurate pe baza de $BaTiO_3$" , Revista Romana de Materiale, **vol. 37**, nr. 3, 2007

[10] *C. Zhao, T. Wang*, "Flux growth and magnetic properties of hexagonal ferrite single crystal", in J. Appl. Phys., **vol. 61**, 2009, pp. 4154 - 4154

[11] *L. Lu, Y.-Y. Song, J. Bevivino, M. Wu*, "Planar Millimeter Wave Notch Filters Based on Magnetostatic Wave Resonance in Barium Hexagonal Ferrite Thin Films", American Physical Society, Annual Meeting of the Four Corners Section of the APS, October 15-16, 2010, abstract **#C2.005**, http://adsabs.harvard.edu/abs/2010APS..4CF.C2005L

[12] *A. Yang, Y. Chen, Z. Chen, C. Vittoria, V. G. Harris*, "Magnetic and atomic structure parameters of Sc-doped barium hexagonal ferrites", in J. Appl. Phys., **vol. 103**, 2008, pp. 07E511

[13] *F. J. Rachford, D. N. Armstead, V. G. Harris, C. Vittoria*, "Simulations of Ferrite-Dielectric-Wire Composite Negative Index Materials", in Phys. Rev. Lett., **vol. 99**, 2007, pp. 057202 [4 pages]

[14] *V. G. Harris, A. Geiler, Y. Chen, S. D. Yoon, M. Wu, A. Yang, Z. Chen, P. He, P. V. Parimi, X. Zuo, C. E. Patton, M. Abe, O. Acher, C. Vittoria*, "Recent advances in processing and applications of microwave ferrites", in J. Magn. Magn. Mater., **vol. 321**, 2009, pp. 2035-2047.

[15] *C. Stan, C., C.P. Cristescu, M., Balasoiu, N. Perov, V.N Duginov, T.N. Mamedov, L., Fetisov, L., "*Investigations of a Fe3O4-ferrofluid at different temperatures by means of magnetic measurements" in UPB Sci. Bull., Series A: Applied Mathematics and Physics, **73**, 2011,. pp. 117-124

[16] *C. Stan, D. E. Creanga, C. P. Cristescu, M. Racuciu*, "Magnetogranulometric characteristics and fractal type dispersion within an aqueous ferrofluid based on magnetite stabilized with tetramethyl amonium hydroxide", Bul. Inst. Politeh. Iaşi, Secţ. I, Mat. Mec. Teor. Fiz., Tom LVI (LX) Fasc. 4, 2010, pp. 153-158.