Grant Information

Grant Number	HR0011-09-1-0047
Title of Research	Nanoscale Engineering of Multiferroic Hybrid Composites for Micro- and Nano-scale Devices
Principal Investigator	Dr. Charles J. O'Connor
Organization	University of New Orleans, New Orleans, LA 70148

Final Technical Report September 14, 2012

1. Objectives:

- Develop a synthetic technology of lead-free high frequency multiferroic composites
- Develop a method of fabrication of arrays of free-standing magnetoelectric or multiferroic composites.
- Investigate wet chemistry synthesized multiferroic nanomaterials (nanoparticles, nanowires, nanotubes, etc.) using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to study their correlation between morphologies, composition, assembly, etc. and synthesis conditions. Meanwhile, e-beam *in-situ* nanolithography has been developed for multiferroic related devices fabrication.
- Fabricate spinel and perovskite pristine phases with controllable composition and dimensionality and use them as building blocks to design magnetoelectric ceramic nanocomposites with integrated functionalities
- Demonstrate that the direct ME effect can be measured at nanometer-length scale by detecting the changes in the piezoresponse of a multiferroic material when subjected to the action of a magnetic field.
- Mapping of the ME coupling through the domain imaging,
- Estimate quantitatively the ME coupling coefficient
- Understand the fundamental physics of magnetoelectric interactions at nanoscale for implementation of multiferroic materials into functional devices.

Co-PI: Dr. Leszek Malkinski w/ Postdoc Dr. N. Babu

Brief Narrative:

Some of major problems with applications of multiferroic composites are: lead content, relatively large losses at microwave frequencies and a clamping effect. Therefore, our group research was focused on technology of new lead-free multiferroic composites suitable for high-frequency applications and on design of thin film materials which minimizes the stray effect of clamping of the composite by the substrate.

Research Progress:

To realize the first objective a series of NBT-CFO ($Na_{0.5}Bi_{0.5}TiO_3/CoFe_2O_4$)granular multiferroic composites with 0-3 connectivity have been prepared by solid state sintering method. The volume fraction of the of the piezoelectric phase varied from 55% to 85%. The magnetic and piezoelectric properties as well as magnetoelectric properties have been carefully characterized. A record number of converse magnetoelectric coefficient of 109 Oe cm/kV was found in the sample with intermediate (30%) content of Co-ferrite [publications 3,5]. The effect of the electric field on ferromagnetic resonance curves is presented in Fig.1. In the case of laminate structures we proposed to use AlN as a piezoelectric phase [publication 4]. Although commonly used Pb-based PZT has superior piezoelectric performance it shows much larger losses at microwave frequencies than AlN. We fabricated bi-layer aluminum nitride (AlN)/cobalt iron (CoFe) magnetoelectric (ME) thin films using reactive rf/dc magnetron sputtering. The bi-layer thin film exhibited both good piezoelectricity and ferromagnetism, as well as ME effect. A 52% change observed in the piezoelectric signal (Fig.2.), measured using magnetic field assisted piezoresponse force microscopy, can be ascribed to the existence of a stress-mediated magnetoelectric coupling between AlN and CoFe. Finally, in order to reduce or eliminate the clamping effect in magnetoelectric composites we used stress engineering to fabricate free-standing magnetoelectric composites in the form of double microtubes [publication 4]. We used a new type of sacrificial layer (copper) to grow galfenol/aluminum/nitride films with 5 nm Au protective layers. The growth-induced stresses between GaFe and AlN layers caused rolling of the rectangular film patterns when they were released from the sacrificial layer by selective etching of the Cu underlayer. The optical image of the array of the scrolled magnetoelectric film patterns

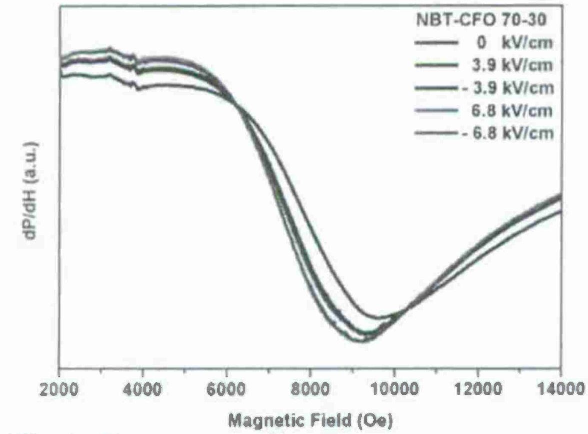

Fig.1. Ferromagnetic resonance curves of Co-ferrite in granular composites measured at different electric fields

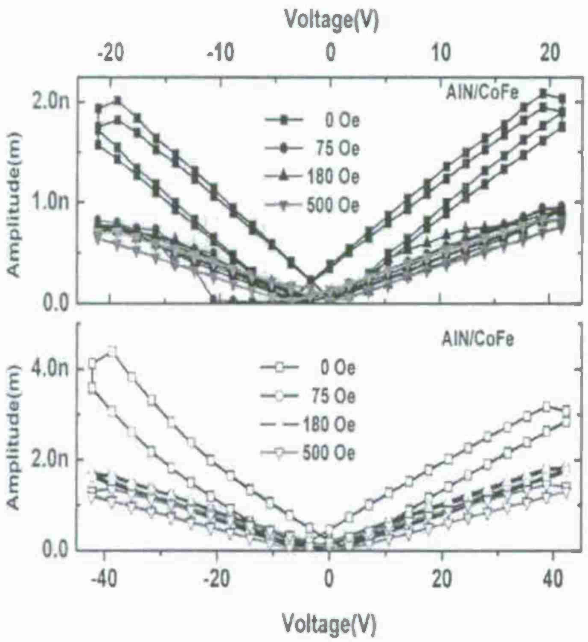

Fig. 2.The piezoelectric response amplitude variations with applied bias magnetic field, with driving voltage of V =622.4 and642.24 V, for AlN=CoFe bilayer

and the scanning electron microscope image of the magnified single structure are illustrated in Fig.3.

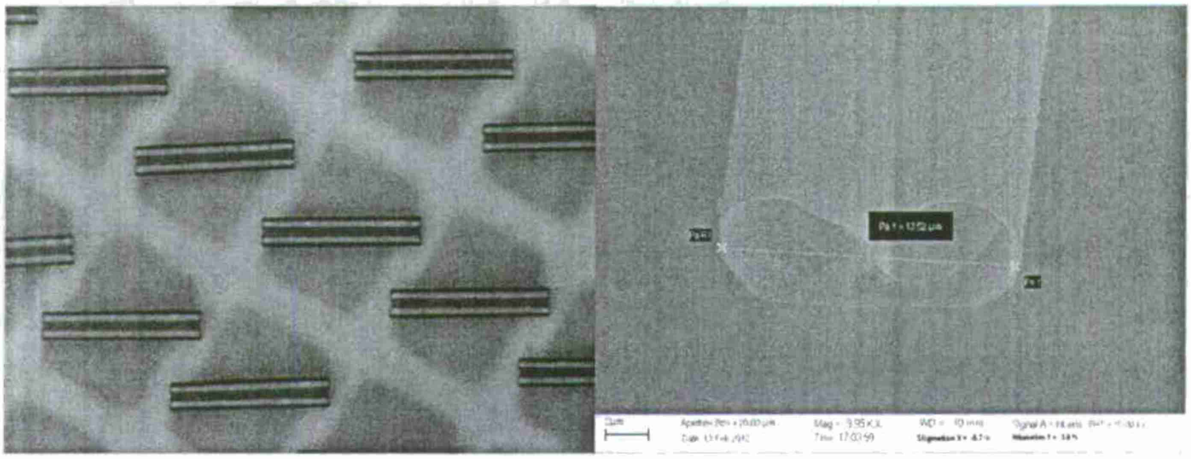

Fig.3. An array of “double barrelled shotgun” magnetoelectric structures Au(5 nm)/AlN(20 nm)/CoFe(40 nm)/Au(5 nm) (SEM image of the tube on the right)

The research on multiferroic composites resulted in a discovery of a new biomedical application of multiferroic nanoparticles. This concept was a subject of UNO Technology disclosure and was published as a book chapter [publication 1]. Co-PI received additional funding from NSF EAGER grant to continue research on this problem.

Co-PI: Dr.Weilie Zhou

Research Progress:

1. We observed free-standing, cubic-like monodispersed BaTiO3 nanocrystals with well-defined shape, controllable size and a high degree of compositional homogeneity, which are essential for the study of the ferroelectricity at nanoscale, as well the possibilities to assemble individual nanoparticles into functional nanostructures, such as 3D ferroelectric crystals and magnetoelectric multiferroic superlattices.

2. In-situ nanolithography and measurement techniques under a field emission scanning electron microscope (FESEM) have attracted significant attention of many researchers since they provide facile ways to precisely pattern nanostructures for specific device fabrication, and measure the various characteristics (e.g. electrical and mechanical properties) of nanostructures without complicated sample preparation, respectively. In this work, in-situ nanolithography technique has been developed with great positioning accuracy for nanodevice fabrication. The positioning errors can be minimized to about 10 nm even without a high precision SEM stage, which is sufficient for most device fabrication. The simplified process can provides an easy, low cost and

less time consuming route to integrate nanomanterials based structures using a converted FESEM e-beam system.

Co-PI: Dr. Gabriel Caruntu

Brief Narrative:

The magneto-electric effect that occurs in some multiferroic materials is fully described by the magneto-electric coupling coefficient induced either electrically or magnetically. This is rather well understood in bulk multiferroics, but it is not known whether the magneto-electric coupling properties are retained at nanometer length scales in nano-structured multiferroics. The main challenges are related to measurement difficulties of the coupling at nanoscale, as well as the fabrication of suitable nano-multiferroic samples. Addressing these issues is an important prerequisite for the implementation of multiferroics in future nanoscale devices and sensors. In this paper we report on the fabrication of two ceramic nano-composite multiferroic samples with a perovskite as the ferroelectric phase and two different ferrites (cubic spinel and hexagonal) as the magnetic phases. The measurement of their magneto-electric coupling coefficients at nanoscale has been performed using a magnetic field-assisted piezoelectric force microscopy technique. The experimental data has been analyzed using a theoretical relation linking the piezoelectric coefficient to the magneto-electric coupling coefficient. Our results confirm the presence of a measurable magneto-electric coupling at nanoscale. The reported values as well as our theoretical approach are both in good agreement to previously published data for bulk and nanostructures magnetoelectric multiferroics.

1. **Research Progress:**

The PFM phase contrast image of the bilayered structure without poling the sample (Figure 2a) reveals the existence of randomly distributed bright and dark areas corresponding to parallel and antiparallel orientation of the polarization mapped by the piezoelectric response due to the tensor element d_{33} associated with ferroelectric domains all across the film surface (3 x 3 μm^2). As it can be noticed from the phase contrast images of the out-of-plane piezoresponse, when the magnetic applied field is varied from H= -600 Oe to + 600 Oe the dark areas, which correspond to electric dipoles oriented downward, nucleate and grow at the expense of domains where polarization is oriented to the film surface (bright areas). This result suggests that the polarization can be switched in an opposite direction when an in-plane magnetic field is applied to the PTO-NFO bilayered nanocomposite as the result of a stress-mediated ME coupling between the ferrite and the perovskite layers. Figure 4 shows the phase and amplitude plots of the piezoresponse corresponding to the PTO-NFO bilayered structure in applied magnetic field. The amplitude signal displays the well-known "butterfly"-type aspect characteristic of a ferroelectric material. Figure 3a indicates that the piezoresponse phase hysteresis loops change their orientation at magnetic applied fields larger than 600 Oe. The change of 179° of the phase signal when the bias voltage was swept from -22 to +22 V is associated with the existence of 180° domain structures in the PTO layers. The dominance of 180° domain structures of the dielectric dipoles in the out-of-plane direction is also suggested by the linearity of the amplitude loops of the piezoelectric signal. The hysteresis loops are asymmetric with respect to the origin, presumably due to a small imprint [1-3], the different barrier potential between the electrode and the film [4], pinning of the domain walls by defects [3] or the presence of an internal electric field inside the film[5]. Moreover, the phase loops are shifted when the magnetic field is increased from 0 to 2000 Oe, but their variation is random, similar to the case described recently by Xie and coworkers for CFO-PZT core-shell nanofibers[6]. Since the phase of the piezoresponse is related to the orientation of the ferroelectric domains, we can reasonably ascribe this change in the orientation of the phase hysteresis loops to the polarization change of the $PbTiO_3$ layer due to the stress produced by adjacent ferrite layer at a critical value of the applied magnetic field. The phase curves are asymmetric with respect to the zero bias line (Figure 5a), being shifted to negative values with coercivities for the local switching of 9.1, 9.7, 7.7, 9.9, 7.9 and 7.4 V, respectively. The amplitude curves displayed in Figure 5b show a hysteretic behavior and their becomes steeper when the magnetic field was swept from 0 to 2000 Oe, thereby suggesting that the piezoelectric coefficient of the PTO-NFO bilayered nanocomposites is magnetic field dependent.

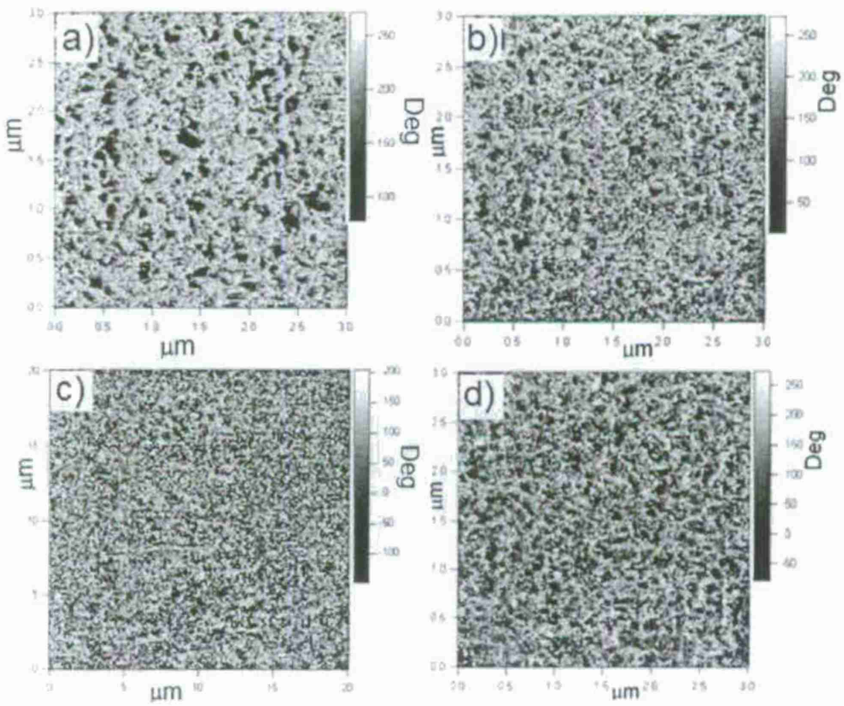

Figure 4. Piezoresponse images of the PTO-NFO bilayered composite under a magnetic field parallel to the plane of the film and different magnitudes H= -600 Oe (a), 0 Oe (b) , +300 Oe (c) and =600 Oe (d), respectively

In order to rule out possible experimental artifacts, a PTO test-layer deposited under the same conditions on the $LaNiO_3$-buffer (100) was probed by PFM in applied magnetic field. No noticeable change of the slope of the measured piezoresponse amplitude has been detected, which confirms that such behavior is intrinsic, being the result of the electromechanical coupling between the magnetostrictive and piezoelectric layers in the nanocomposite.

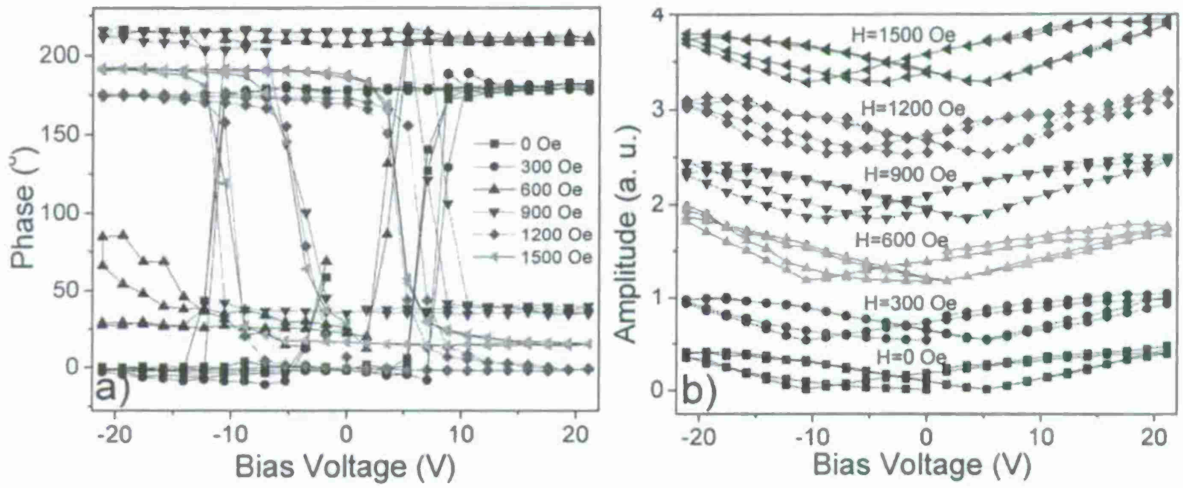

Figure 5. Phase (a) and amplitude (b) curves of the piezoresponse of the PTO-NFO bilayered structure under different magnetic fields. In Figure 2b the plots have been translated vertically to increase their visibility

When the ac electric field is applied through the conductive tip, the ferroelectric layer will start vibrating at the same frequency as a result of the converse piezoelectric effect. The characteristic amplitude at which the electrostrictive layer vibrates is proportional to the piezoelectric coefficient d_{ij}: $A=\delta d_{ij}V_{ac}$ (2). In Eq. (2) the constant δ is the sensitivity of the optical detector; that is a proportionality factor that accounts for the amplitude enhancement at the tip-sample resonance, whereas V_{ac} is the testing voltage. From the magnetic field-induced piezoelectric deformation of the samples we calculated the values of the transversal piezoelectric coefficient d_{31}. These are 25.9, 36.7, 39.8, 45.7, 54.7 and 59.6 pm/V for a magnetic field of 0, 300, 600, 900, 1200 and 1500 Oe. It can be inferred that the transversal piezoelectric coefficient increases linearly with the magnetic field, with a positive slope reaching a maximum value at 1500 Oe, which corresponds to the saturation field of the nickel ferrite layer [7]. The ME coupling coefficient is conventionally defined as $\alpha_{ME}=\frac{\partial E}{\partial H}$ (5), where E and H denote the electric and magnetic fields. The polarization in a dielectric material is proportional to the electric field $P=\varepsilon_{31}E_3$ (6) where ε_{31} is the in-plane component of the dielectric permittivity tensor. In ferroelectrics with a centrosymmetric paraelectric phase, such as $PbTiO_3$ the piezoelectric effect may be considered as the electrostrictive effect biased by the spontaneous polarization: $d_{31}=2\varepsilon_{31}QP$ (7), where Q is the electrostrictive coefficient. By combining equations (5), (6) and (7) we obtain the mathematical relationship which allows the quantitative determination of the direct ME coupling coefficient for any type of connectivity scheme between the two constituent phases from the variation of the of the piezoelectric coefficient with the magnetic field:

$$\alpha_{ME}=\frac{1}{2\varepsilon_{31}^2Q}\frac{\partial(d_{31})}{\partial H} \quad (8)$$

By using the bulk value for the dielectric constant ($\varepsilon \approx 1200$)[8] of $PbTiO_3$ we obtained values of the ME coupling coefficient of 435.3 mV/cm•Oe for the $PbTiO_3$- $Ni_{0.66}Fe_{2.34}O_4$

bilayered nanostructures, respectively. The obtained values are in line with those reported in the literature for particulate perovskite ferrite ME nanocomposites [9-11] indicating a very good coupling between the PTO and the ferrite layers in our nanocomposites. Since the mechanical stress σ_3 in a piezoelectric material is defined as[12]: $\sigma_3 = \frac{-E_3}{g_{31}}$ (9) and $g_{31} = \frac{d_{31}}{\varepsilon_{31}}$ (10), where g_{31} and d_{31} and piezoelectric coefficients, by combining (8) with (9) and (10) we obtain:

$$\alpha_{ME} == -\frac{\sigma}{\varepsilon_{31}} \frac{\partial(d_{33})}{\partial H} \quad (11)$$

which is the expression proposed by Vopsaroiu *et al.*[13]. This shows that our equation and that obtained by Vopsaroiu *et al.* are equivalent, which furthermore validates furthermore the proposed model for the quantitative and qualitative measurement of the ME coupling coefficient from magnetic field-assisted PFM measurements.

References

[1] X. S. Gao, *et al.*, "Microstructure and Properties of Well-Ordered Multiferroic Pb(Zr,Ti)O-3/CoFe2O4 Nanocomposites," *Acs Nano,* vol. 4, pp. 1099-1107, Feb.

[2] A. Gruverman, *et al.*, "Nanoscale observation of photoinduced domain pinning and investigation of imprint behavior in ferroelectric thin films," *Journal of Applied Physics,* vol. 92, pp. 2734-2739, 2002.

[3] Z. Wang, *et al.*, "Ferroelectric and piezoelectric behaviors of individual single crystalline BaTiO[sub 3] nanowire under direct axial electric biasing," *Applied Physics Letters,* vol. 89, pp. 082903-3, 2006.

[4] D. Damjanovic, "Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics," *Reports on Progress in Physics,* vol. 61, p. 1267, 1998.

[5] V. V. Shvartsman, *et al.*, "Piezoelectric Properties of Self-Polarized Pb(Zr_xTi_{1-x})O₃ Thin Films Probed by Scanning Force Microscopy," *Integrated Ferroelectrics: An International Journal,* vol. 69, pp. 103 - 111, 2005.

[6] S. Xie, *et al.*, "Multiferroic CoFe2O4-Pb(Zr0.52Ti0.48)O3 core-shell nanofibers and their magnetoelectric coupling," *Nanoscale,* 2011.

[7] A. Yourdkhani, *et al.*, "Magnetoelectric Perovskite-Spinel Bilayered Nanocomposites Synthesized by Liquid-Phase Deposition," *Chemistry of Materials,* vol. 22, pp. 6075-6084, Nov 2010.

[8] J. Kobayashi, *et al.*, "Dielectric Behavior of Lead Titanate at Low Temperature," *Physical Review,* vol. 103, p. 830, 1956.

[9] G. Sreenivasulu, *et al.*, "Magnetoelectric effect of (100-x)BaTiO3-(x)NiFe1.98O4 (x=20-80 wt %) particulate nanocomposites," *Applied Physics Letters,* vol. 94, Mar 2009.

[10] R. A. Islam, *et al.*, "Piezoelectric transformer based ultrahigh sensitivity magnetic field sensor," *Applied Physics Letters,* vol. 89, Oct 2006.

[11] R. A. Islam, *et al.*, "Magnetoelectric properties of core-shell particulate nanocomposites," *Joumal of Applied Physics,* vol. 104, Nov 2008.
[12] D. Damjanovic, "Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics," *Reports on Progress in Physics*, vol. 61, pp. 1267-1324, Sep 1998.
[13] M. Vopsaroiu, *et al.*, "Experimental determination of the magnetoelectric coupling coefficient via piezoelectric measurements," *Measurement Science & Technology*, vol. 19, Apr 2008.

Publications: 2009-2012

1) Adireddy, S.; Lin, C.; Palshin, V.; Cole, R.; Caruntu, G. "Size-Controlled Synthesis of Quasi-Monodisperse Transition-Metal Ferrite Nanocrystals in Fatty Alcohol Solutions" J. Phys. Chem. C. 2009, 113, 20400.

2) Adireddy, S.; Lin, C.; Zhou, W..; Cao, B., Caruntu, G. "Solution-Based Growth of Monodisperse Cube-Like BaTiO3 Coloidal nanocrystals" Chem. Mater. 2010, 22, 1946.

3), L. Malkinski, M. Yu, D. Scherer II Magnetostatic interactions of two-dimensional arrays of magnetic strips MRS Proceedings 1250: 1250-G08-03 II (2010), Cambridge University Press 2010.

4) D. Mohanty, Chaubey, G.; Yourdkhani, A.; Adireddy S.; Caruntu, G.; Wiley, J. B. "Synthesis and piezoelectric response of cubic and spherical $LiNbO_3$ nanocrystals" RSC Advances 2012, 2, 1913.

5) Yourdkhani, A.; Perez, A., K.; Lin, C.; Caruntu G."Magnetoelectric Bilayered Nanocomposites Prepared by Liquid Phase Deposition", Chemistry of Materials, 2010, 22(6), 6075.

6) Yourdkhani, A.; Caruntu, G. "Highly ordered transition metal ferrite nanotube arrays synthesized by template-assisted liquid phase deposition" J. Mater. Chem. 2011, 21, 7145.

7) Yourdkhani, A.; Caruntu, G. "Characterization of the Microstructural and Piezoelectric Properties of $PbTiO_3$ Thin Films Synthesized by Liquid-Phase Deposition:, Article ASAP, J. Phys. Chem. C 2011, 115, 14797.

8) Yourdkhani, A.; Gazra, E.; Zaldivar, L.; Spinu, L; Caruntu, G. "Magnetic Field-Assisted Piezoresponse Force Microscopy Investigation of PbTiO3-TbDyFe Bilayered Nanocomposites" IEEE Trans. Magn. 2011, 47(10),

9) J._Vargas, J.; Srivastava, A; Yourdkhani, A.; Zaldivar, L.; Caruntu, G.; Spinu, L. "Tuning the thermal relaxation of transition metal ferrite nanoparticles through their intrinsic magnetocrystalline anisotropy" J. Appl. Phys. 2011. 34

10) S. Min, J.H, Lim, J. Gaffney, K. Kinttle, J. B. Wiley, L. Malkinski, "Fabrication of scrolled magnetic thin film patterns", J. Appl. Phys.,**111**, 07E518 ((pp.1-3) (2012)

11) S.N. Babu and L. Malkinski, "Large converse magnetoelectric effect in $Na_{0.5}Bi_{0.5}TiO_3$-$CoFe_2O_4$ lead-free multiferroic composites" , J. Appl. Phys. **111**, 07D919 (p.1-3)(2012).

12) S.N. Babu, S.G. Min, A. Yourdkhani, G. Caruntu, and L. Malkinski, "Magnetoelectric effect in AlN/CoFe bi-layer thin film composites", accepted for publication in J. Appl. Phys.

14) A. Kargol, L. Malkinski and G. Caruntu "Biomedical Applications of Multiferroic Nanoparticles" accepted to "Magnetic Material" (28 pages) in "Magnetic Material",editor-L. Malkinski, INTECH 2011, ISBN 979-953-307-547-0 (in progress)

15) S. Min, J.H, Lim, J. Gaffney, K. Kinttle, J. B. Wiley, L. Malkinski, "Fabrication of scrolled magnetic thin film patterns", J. Appl. Phys.,111, 07E518 ((pp.1-3) (2012)

16) S.N. Babu and L. Malkinski, "Large converse magnetoelectric effect in $Na_{0.5}Bi_{0.5}TiO_3$-$CoFe_2O_4$ lead-free multiferroic composites" , J. Appl. Phys. 111, 07D919 (p.1-3) (2012)

17) S. N. Babu, S-G. Min, and L. Malkinski, "Electric field tunable magnetic properties of lead-free $Na_{0.5}Bi_{0.5}TiO_3/CoFe_2O_4$ multiferroic composites". *J. Appl. Phys*. 109, 07D911 (2011)

18) S.N. Babu, S.G. Min, A. Yourdkhani, G. Caruntu, and L. Malkinski, "Magnetoelectric effect in AlN/CoFe bi-layer thin film composites", J. Appl. Phys.,111, 07C720 (pp.1-3) (2012)

19) Caruntu, G.; Yourdkhani, A.; Caruntu, G.; Vopsaroiu, M.; Srinivasan, G. Probing the local strain-mediated magnetoelectric coupling in multiferroic nanocomposites by magnetic field-assisted piezoresponse force microscopy" Nanoscale, *Nanoscale*, **2012**, *4*, 3218.

20) Babu, N.; Min S. G.; Yourdkhani A.; Caruntu, G.; Malkinski L. "Magnetoelectric Effect in AlN/CoFe Bilayer Thin Film Composites" J. Appl. Phys. 2012, 111, 07C720.

21) Yourdkhani, A._; Gazra, E.; Zaldivar, L.; Spinu, L; Caruntu, G "Magnetic Field-Assisted Piezoresponse Force Microscopy Investigation of PbTiO3-TbDyFe Bilayered Nanocomposites" IEE Trans. Magn. 2011, 47(10),

22) Polking, M. J.; Han, M. G.; Yourdkhani, A.; Petkov, V.; Kisielowski, C. F.; Volkov, V. V.; Zhu, Y.; Caruntu G.; Alivisatos, A. P.; Ramesh R. "Ferroelectric Order in Individual Nanometre-Scale Crystals" *Nature Materials* **2012**, *11*, 700.

23) New Polytypoid SnO2(ZnO:Sn)m Nanowire: Characterization and Calculation of Its Electronic Structure" Baobao Cao, Tingting Shi, Shijian Zheng, Yumi H. Ikuhara, Weilie Zhou, David Wood, Mowafak Al-Jassim, and Yanfa Yan", J. Phys. Chem. C, 116, 5009–5013 (2012).

24) Book chapter: A. Kargol, L. Malkinski and G. Caruntu "Biomedical Applications of Multiferroic Nanoparticles" in "Advanced Magnetic Materials", Intech 2012 ch.4 pp. 89-118 (28 pages).

UNO Technology Disclosure

1) "Application of multiferroic nanoparticles for remote magnetic-field-driven electric signal stimulation of living cells", Leszek Malkinski and Armin Kargol (Loyola University) (2010).

Presentations: 2009-2012

1) Shiva Adireddy, Cuikun Lin, Amin Yourdkhani and Gabriel Caruntu, Materials Research Society (MRS) Fall Meeting, November 30-December 5, 2009, Boston, MA.

2) G. Caruntu, NanoRomania NSF Workshop, June 5-9, 2009 Iasi, Romania.

3) Yourdkhani, A.; Perez, A. K.; Lin, C.; Caruntu, G. "Chemical Design of Multilayered Hybrid Magnetoelectric Nanostructures by Liquid Phase Deposition", Materials Research Society Meeting, Boston, MA, Nov. 30-Dec. 4, 2009. "Microwave absorption of magnetic antidot arrays", L. Malkinski, M. Yu, D. Scherer II, MRS Spring Meeting, April 5-9, 2010, San Francisco, CA.

4) Magnetostatic interactions of two-dimensional arrays of magnetic strips, L. Malkinski, M. Yu, D. Scherer II, MRS Spring Meeting, April 5-9, 2010, San Francisco, CA.

5) Adireddy, S.; Caruntu, G. "Rational Approach to the Sythesis of Ferroelectric BTO Nanocubes with Variable Edge-Lengths", Poster presentation, MRS Spring Meeting, April 5-9, 2010, San Francisco, CA.

6) Gabriel Caruntu, Amin Yourdkhani, Armando K. Perez, Shiva Adireddy "Soft Solution Processing of Ferroelectric Nanostructures and Their Assemblies" American Chemical Society Fall Meeting, Boston, MA, August 22-26, 2010.

7) Amin Yourdkhani, Armando K. Perez, Gabriel Caruntu "Investigation of the Magnetoelectric Coupling in Ceramic Bilayered Nanocomposites by Magnetic Field-Assisted Piezoelectric Force Microscopy" International Workshop for Scanning Probe Microscopy for Energy Applications, Oak Ridge National Laboratory, Oak Ridge, TN, September 15-17, 2010.

8) Narendra Babu.S, Seong Gi-Min, Leszek Malkinski, "Electric field tunable magnetic properties of lead-free $Na_{0.5}Bi_{0.5}TiO_3/CoFe_2O_4$ multiferroic composites", in 55th Annual Conference on Magnetism and Magnetic Materials(MMM-2010), Atlanta, GA, Nov 14-18, 2010

9) Debasish Mohanty, Girija S. Chaubey, Amin Yourdkhani, Gabriel Caruntu, and John B. Wiley. Synthesis and ferroelectric property of $LiNbO_3$ nanostructures. Joint 66th Southwest and 62nd Southeastern Regional Meeting of the ACS, **2010**. (Poster presentation)

10) Debasish Mohanty, Girija S. Chaubey, Amin Yourdkhani, Gabriel Caruntu, and John B. Wiley. Synthesis and characterization of $LiNbO_3$ nanostructures. Materials Research Society Spring meeting, San Francisco, 2011. (accepted for poster presentation).

11) S. Min. L. Malkinski and K. Kim, "Ferromagnetic resonance study of damping in of permalloy thin films sandwiched by insulator" in 55th Annual Conference on Magnetism and Magnetic Materials(MMM-2010), Atlanta, GA, Nov 14-18, 2010.

12) Gabriel Caruntu, Amin Yourdkhani, Armando K. Perez, Shiva Adireddy "Soft Solution Processing of Ferroelectric Nanostructures and Their Assemblies" American Chemical Society Fall Meeting, Boston, MA, August 22-26, 2010.

13) Gabriel Caruntu, Yourdkhani A.; Dagtepe, P. , Adireddy, S.; Perez, A.; Valdez, E.; Zaldivar, L. "Chemical strategies for the controlled synthesis of magnetoelectric nanostructures with variable architectural complexity" South Eastern-South West Regional American Chemical Society Meeting, December, 1-4, New Orleans, LA.

14) Caruntu, G. "Architectural Design of Ferroelectric and Magnetoelectric Nanostructures by Soft Solution Routes", invited talk Louisiana State University, Baton Rouge, LA, March, 24, 2011

15) Caruntu G. "Nanoscale Functional Ferroic Oxides", invited talk Drexel University, Philadelphia, PA, April, 6, 2011

18). G. Caruntu-invited talk at The 20th IEEE International Symposium on Applications of Ferroelectrics International Symposium on Piezoresponse Force Microscopy & Nanoscale Phenomena in Polar Materials, July 27-27, 2011, Vancouver, Canada.

20) Fabricatioin of rolled-up magnetic microtubes, S. Min, J. Gaffney, R. Eskandari and L. Malkinski, MRS Fall meeting Boston, Nov Nov. 28-Dec 2, 2011.

21) Fabrication of scrolled magnetic thin film patterns, S. Min, J.H, Lim, J. Gaffney, K. Kittle, J. B. Wiley, L. Malkinski Magnetoelectric effect in AlN/CoFe bi-layer thin film composites, S. N. Babu, L.

22) Malkinski, 56 Annual Conference on Magnetism and Magnetic Materials Arizona Oct 2012

23) Giant converse magnetoelectric effect in $Na_{0.5}Bi_{0.5}TiO_3$-$CoFe_2O_4$ lead-free multiferroic composites, S. N. Babu and L. Malkinski 56 Annual Conference on Magnetism and Magnetic Materials Arizona Oct 2012

24) Yourdkhani, A.; Caruntu G. Probing the local ME effect by magnetic field-assisted piezoresponse force microscopy", MRS Fall meeting Boston, Nov 2011.

25) Farrar, A. K.; Engman, T.; Adireddy, S.; Caruntu, G.; Tenne, D. A. "BaTiO3 Nanocrystals studied by Raman Spectroscopy" American Physical Society National Meeting, February 27-March 2 2012, Boston, MA.

26) In-situ e-beam nanolithography", Weilie Zhou, 18th International conference of composite and Nano-engineering, July 4-11, 2010, Anchorage, AK.

27)"In-situ nanolithography and In-situ measurement under FESEM", Weilie Zhou International Workshop on Materials Behavior at the Micro- and Nano- Scale, Xi'an, China, June 7-11, 2010

28) "Synthesis and sensing investigation of new coordination compounds nanowires", Kun Yao, Zhijie Li, and Weilie Zhou, The 3rd International Conference on One-dimensional Nanomaterials, December 7-9, 2009, Atlanta, Georgia.

29) "In-situ E-beam Nanolithography for Nanodevice Fabrication", Weilie Zhou, Annual Conference of Chinese Electron Microscopy Society, July 16-19, 2009, Zhengzhou, China.

30)L. Malkinski, "Magnetic heterostructures with convoluted architectures" (invited) 7th Workshop on Multifunctionl Materials, Gamboa, Panama Aug. 4-9, 2012

31)N.B. Simhachalam and L. Malkinski, "Magnetoelectric effect in AlN/CoFe bi-layered thin film composites", 56th Annual Conference on Magnetism and Magnetic Materials, Oct 30- Nov 3, 2011, Scottsdale, AZ

32) S. Min, J. H. Lim, J. Gaffney, K. Knittle, J.B. Wiley and M. Malkinski, "Fabrications of scrolled magnetic thin film patterns", 56th Annual Conference on Magnetism and Magnetic Materials, Oct 30- Nov 3, 2011, Scottsdale, AZ

33) *L. Malkinski*, M. Yu, D. J. Scherer II, Magnetic interactions in 2-dimensional arrays of magnetic stripes", presented at Materials Research Society Meeting Spring 2010, San Francisco, Ca.

34) *L. Malkinski*, M. Yu, D. J. Scherer II, "Microwave absorption of magnetic antidote arrays", presented at Materials Research Society Meeting Spring 2010, San Francisco, Ca.

35) L. Malkinski, "Microwave properties of magnetic nanostructures", Seminar at the University of Wyoming, Laramie, WY, March 6, 2010

36) L. Malkinski, "Voltage control of magnetism in multiferroic composites", Seminar at the Colorado State University, Fort Carlson, Co. March 7, 2010

37) L. Malkinski, "Voltage control of magnetism in multiferroic composites", Seminar at the University of Colorado at Colorado Springs, Colorado Springs, Co. March 8, 2010

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
14-09-2012

2. REPORT TYPE
Final Technical Report

3. DATES COVERED *(From - To)*
Jun 2009-Jun 2012; Sept 2012

4. TITLE AND SUBTITLE
Nanoscale Engineering of Multiferroic Hybrid Composites for Micro- and Nano-scale Devices: Final Technical Report

5a. CONTRACT NUMBER
HR0011-09-1-0047

5b. GRANT NUMBER
HR0011-09-1-0047

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Dr. Charles J. O'Connor

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Advanced Materials Research Institute
University of New Orleans
2000 Lakeshore Drive
New Orleans, LA 70148

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Defense Advanced Research Projects Agency-Contracts Management Office
3701 North Fairfax Drive
Arlington, VA 22203-1714

10. SPONSOR/MONITOR'S ACRONYM(S)
DARPA-CMO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Report is a summary of the overall project objectives which include

- Develop a synthetic technology of lead-free high frequency multiferroic Composites;
- Develop a method of fabrication of arrays of free-standing magnetoelectric or multiferroic composites;
- Investigate wet chemistry synthesized multiferroic nanomaterials (nanoparticles, nanowires, nanotubes, etc.) using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to study their correlation between morphologies, composition, assembly, etc. and synthesis conditions. Meanwhile e-beam in-situ nanolithography has been developed for multiferroic related devices fabrication;
- Fabricate spinel and perovskite pristine phases with controllable composition and dimensionality and use them as building blocks to design magnetoelectric ceramic nanocomposites with integrated functionalities;
- Demonstrate that the direct ME effect can be measured at nanometer-length scale by detecting the changes in the piezoresponse of a multiferroic material when subjected to the action of a magnetic field;
- Mapping of the ME coupling through the domain imaging;
- Estimate quantitatively the ME coupling coefficient;
- Understand the fundamental physics of magnetoelectric interactions at nanoscale for implementation of multiferroic materials into functional devices.

15. SUBJECT TERMS
Nanoscale engineering; Multiferroic composites; Multiferroic materials; Micro-scale devices; Nano-scale devices

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Ildefonso R. DeLeon
a. REPORT	b. ABSTRACT	c. THIS PAGE	UU	13	19b. TELEPHONE NUMBER *(include area code)*
U	U	U			504-280-3258

Standard Form 298 (Rev. 8-98)
... 739.18

20121010070