Alexandru Ioan Cuza University of Iasi,
Institute for Interdisciplinary Research, Science Research Department

Study of the relationship between composition-microstructure-functional properties and applications in systems based on ferroelectric perovskites

Results and perspective

CSII dr. Cristina-Elena CIOMAGA

E-mail: cristina.ciomaga@uaic.ro

DIELECTRICS
FERROELECTRICS
& MULTIFERROICS
GROUP

MAIN RESEARCH TOPICS

Ferroelectrics Relaxors

$BaTiO_3$

- $BaTiO_3$ – based solid solution ceramics (ferroelectric – relaxor crossover, tunability, grain boundary, O_2 vacancy effect, FORC method)

Composite

Porous

- Porous Nb-PZT, $BaTiO_3$ - solid solution ceramics (porosity effect on electrical properties)

CNT

- Ferroelectric – CNTs composites by SPS

PZT

BT

- Ferroelectric ($Pb(Zr,Ti)O_3$, $BaTiO_3$) – based magnoelectric composites
- other composite systems

Outlook

I. Introduction

- ➢ Ferroelectrics, Composite materials
- ➢ Applications

II. Main results on

- ➢ **Ferroelectrics**
- ➢ **Ferroelectric-based composites**
- ➢ **Magentoelectric composites**

III. Conclusions

- **Perspectives**

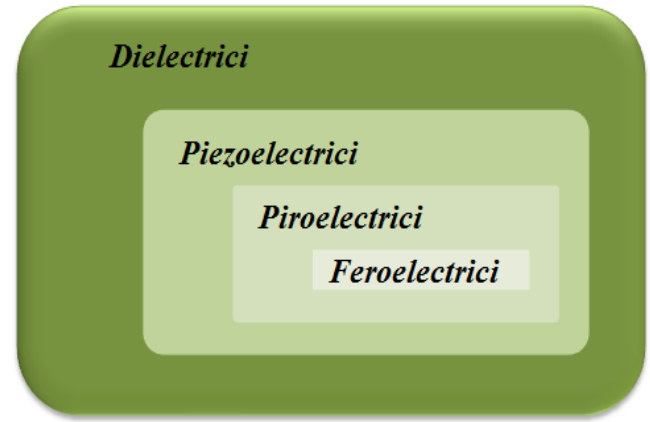
I. Generalities about ferroelectrics

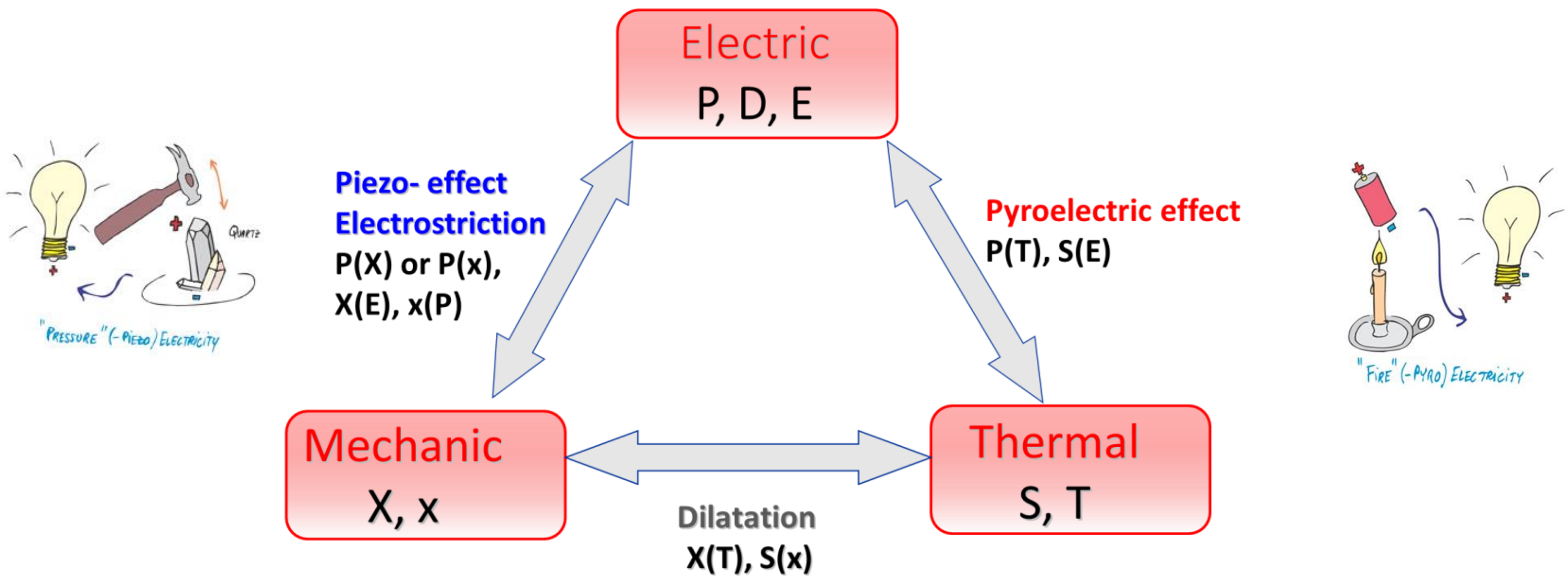
History:

➢*Piroelectricity*: 1824 - David Brewster

➢*Piezoelectricity*: 1880 - Pierre and Jacque Curie

➢*Feroelectricity*: 1920 – Joseph Valasek

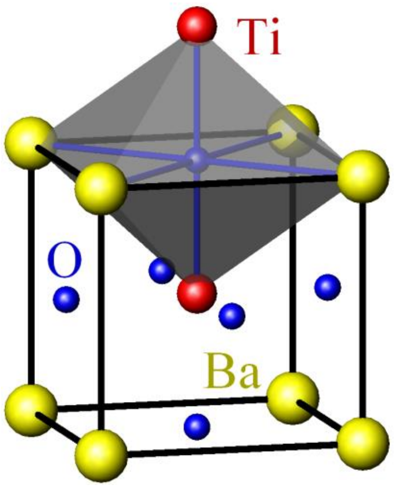


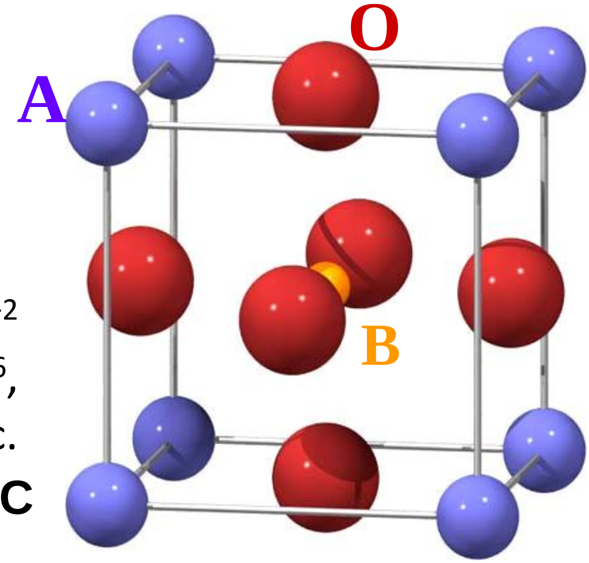


Ferroelectric = multifunctional material

I. Perovskite structure ABO_3

$BaTiO_3$

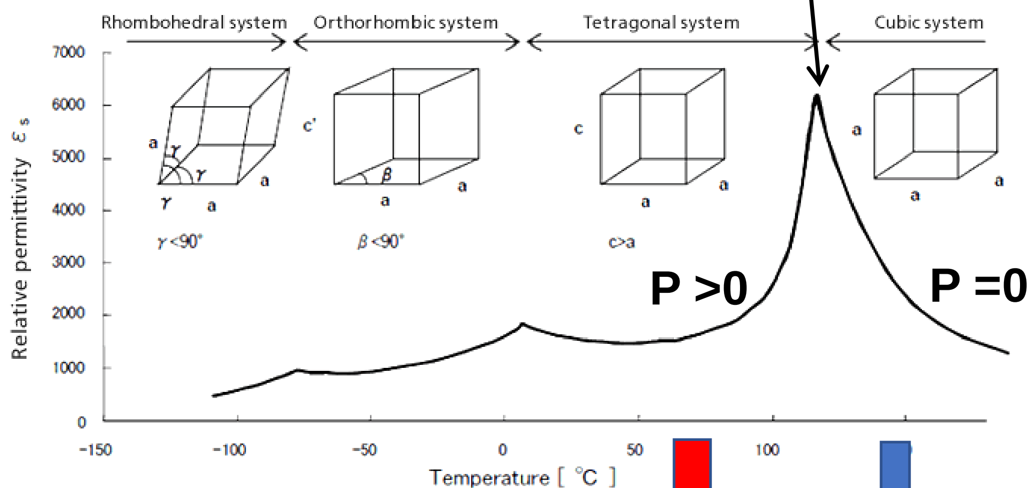




A= Na^{+}, K^{+}, Ca^{+2}, Ba^{+2}, Pb^{+2}

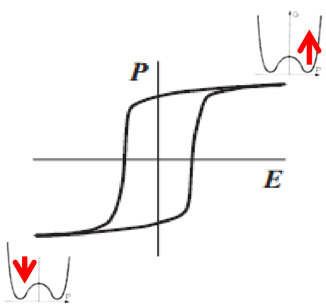
B=Ti^{+4}, Zr^{+4}, Sn^{+4}, Hf^{+4}, Nb^{+5}, Ta^{+5}, W^{+6}, etc.

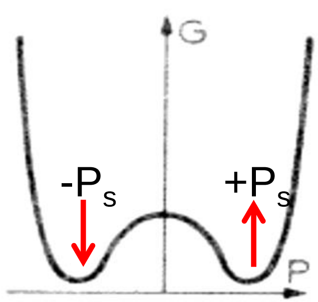
T_C = 120°C

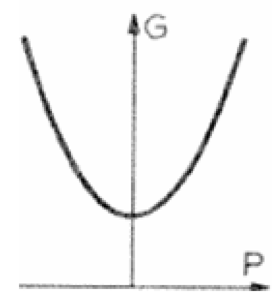


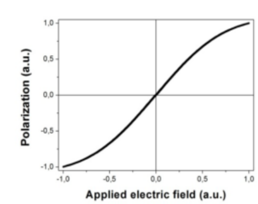
Feroelectric phase

Paraelectric phase









I. Composite materials

A ***composite material*** **is a macroscopic combination of two or more distinct materials that remain separate and distinct while forming a single component.**

Depending on their origin:

- **Natural (biomaterials) composites**;

- **Artificial *("engineered materials")* composites.**

Design to improve mechanical, thermal, optical, electrical, magnetic etc. in order to extend the applicability area.

MATRIX + **Filler** = **COMPOSITES**

MATRIX:
- Ceramic-matrix composites
- Metal-matrix composites
- Organic-matrix composites

Filler:
- Particulate-reinforced composites
- Fiber-reinforced composites
- Structural composites

I. Composite materials

<u>Idea:</u> (1972) 2 phases individually *not* showing a property can achieve it, if appropriately combined or coupled in a composite.

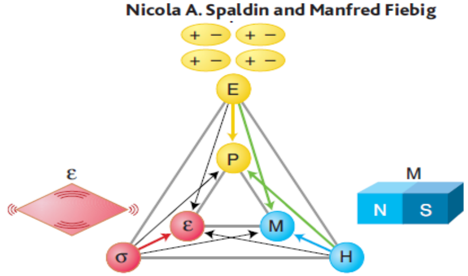
J. Van Suchetelene, Philips Res. Rep. 27, 28 (1972)

Magnetoelectric (ME) composites coupling via magnetostrictive-piezoelectric effect:

MATERIALS SCIENCE

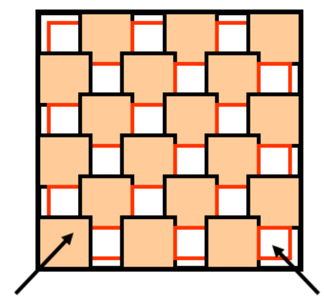
The Renaissance of Magnetoelectric Multiferroics

Nicola A. Spaldin and Manfred Fiebig



Phase control in ferroics and multiferroics. The electric field E, magnetic field H, and stress σ control the electric polarization P, magnetization M, and strain ε, respectively. In a ferroic material, P, M, or ε are spontaneously formed to produce ferromagnetism, ferroelectricity, or ferroelasticity, respectively. In a multiferroic, the coexistence of at least two ferroic forms of ordering leads to additional interactions. In a magnetoelectric multiferroic, a magnetic field may control P or an electric field may control M (green arrows).

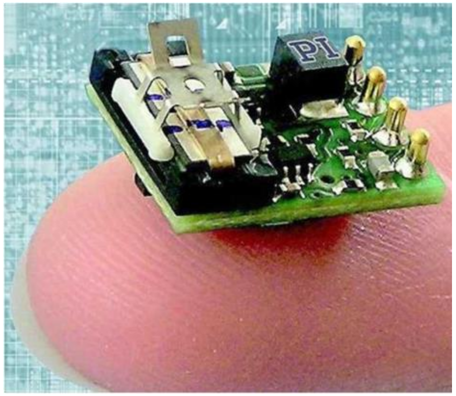
Science 15, 5733 (2005)



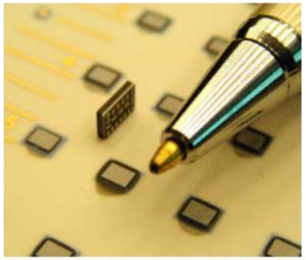
$$ME = \frac{magnetic}{mechanical} \times \frac{mechanical}{electric}$$ → P(H)

$$EM = \frac{electric}{mechanical} \times \frac{mechanical}{magnetic}$$ → M(E)

➢ Applications



➢ Piezo-, pyroelectric sensors



Fully Encapsulated Multi-Chip Module

➢ Microwave antennas

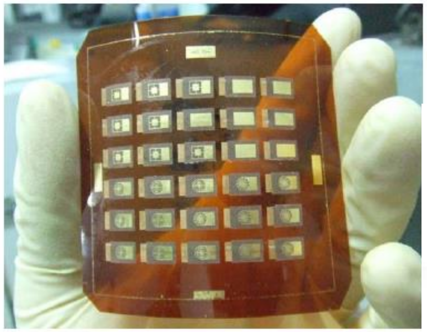
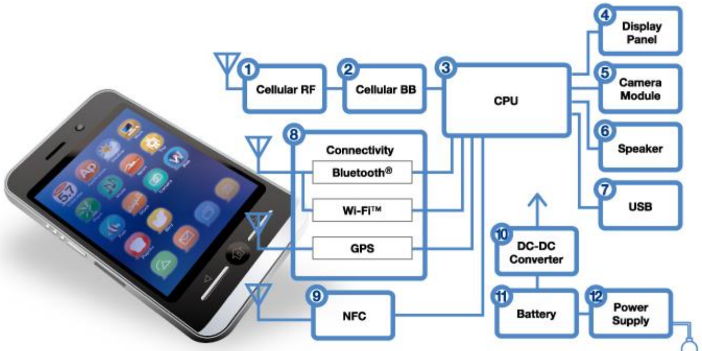


Fig. 3 The photos of the flexible PZT Pyroelectric sensors.



➢ Sensors and Pressure switching

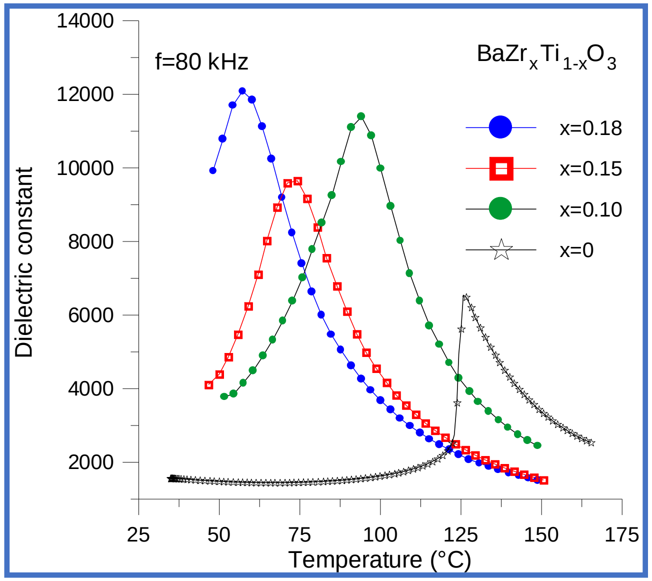
II. MAIN RESULTS

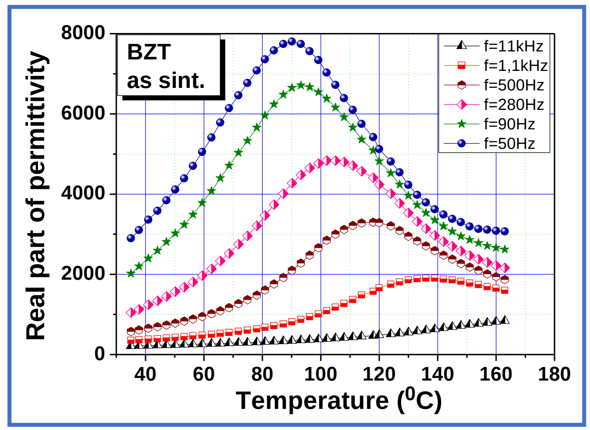
collaboration with ICMATE-CNR Genoa, Italy - Prof. dr. P. Nanni
Dr. V. Buscaglia, Dr. M.T. Buscaglia;
Coord by prof. L. Mitoseriu, Faculty of Physics, UAIC

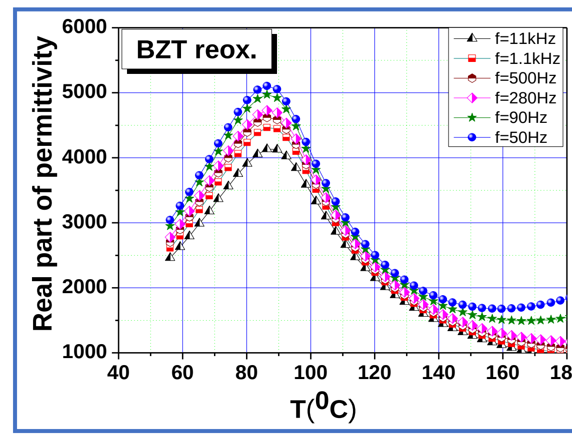
➢ Ferroelectrics

- **Contribution to the study of $BaZr_xTi_{1-x}O_3$ (BZT) ferroelectric-relaxor ceramics**

• C. E. Ciomaga, PhD Thesis, Univ. Al.I. Cuza Iasi, 2006
Suma cum laudae
- **I[st] prize in 2007 for the best PhD Thesis in Physics** at "Al. I. Cuza" Univ. of Iasi, Romania







- GS down to 0.75 µm

➢ *Giant relaxation related to the O-deficiency*

•C.E. Ciomaga et al., Phase Trans. 79, 389 (2006); C. E. Ciomaga et al., J. Opt. Adv. Mat. 8, 944 (2006); C. E. Ciomaga et al., J. Eur Ceram. Soc 27, 4061 (2007); L. Mitoseriu, C. Ciomaga et al., J. Optoel. & Adv. Mater. 10, 1843 (2008); C.E. Ciomaga et al., J. Optoel. & Adv. Mater. 10, 2367 (2008); D. Ricinschi, C.E. Ciomaga et al., J. Eur. Ceram. Society 30, 237 (2010)
• C.E. Ciomaga et al. J. Appl. Phys. 110, 114110 (2011); M. Deluca et al. J. Appl. Phys. 111, 084102 (2012); M. Deluca et al., J. Eur. Ceram. Society (2012)

❑ **Grant of CNCSI S-Ministry of Education and Research of Romania, Grant type BD code 108** - The individual research grants for PhD Students, title: "Contribution to the study of ferroelectric relaxors" (2003-2006)

II. MAIN RESULTS

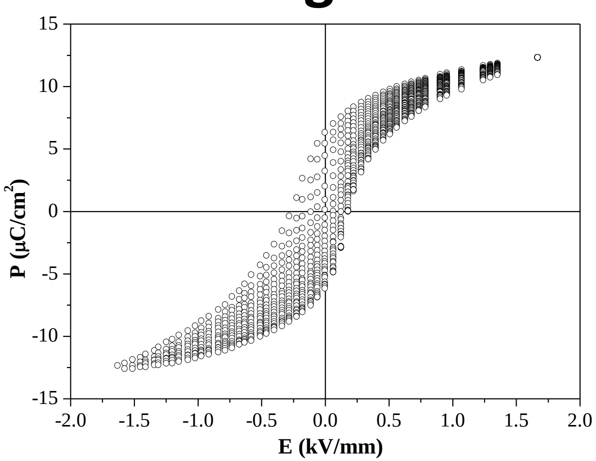
- collaboration with ISTEC-CNR Faenza, Italy, Dr. C Galassi
- Prof.dr. L Stoleriu, Faculty of Physics, UAIC

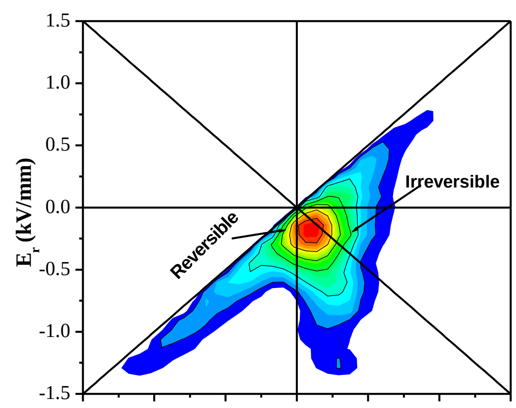
➢ Ferroelectrics Relaxors

- **Ferroelectric-relaxor crossover induced by the B-site substitution in $BaM_{1-x}Ti_xO_3$ (*M*=Zr, Sn, Ce) ceramics**

➢ **Study of ferroelectric-relaxor crossover in $BaZr_xTi_{1-x}O_3$ (BZT) when increasing *x* by first order reversal curves (FORC) method and modeling.**

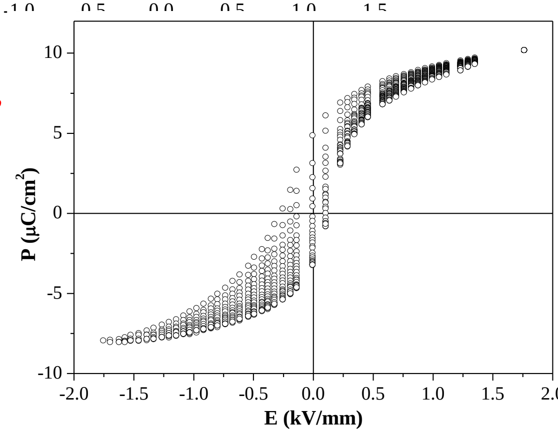
$BaZr_{0.1}Ti_{0.9}O_3$

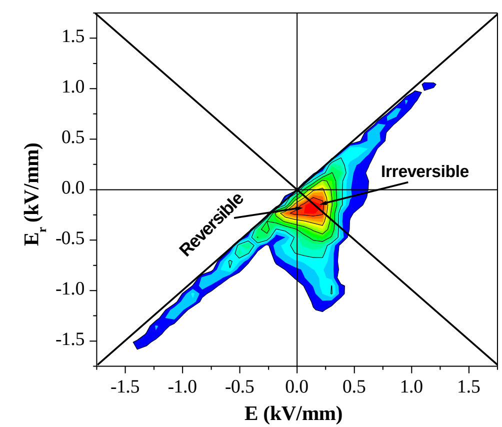




➢ *FORCs indicate the ferroelectric - relaxor crossover when increasing x (progressive reducing of the irrev. component).*

$BaZr_{0.15}Ti_{0.85}O_3$





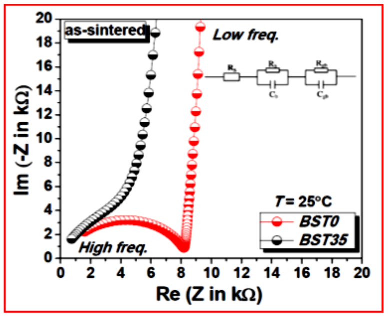
- Mitoseriu, L; Ciomaga, CE; et.al., J. Eur. Ceram. Soc. 27 (13-15), (2007) 3723-3726
- Ianculescu A., Mitoseriu L., Bereger D., Ciomaga CE. Et al, Phase Trans 79, 375-388 (2006)

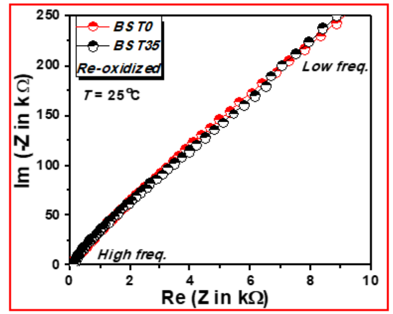
II. MAIN RESULTS

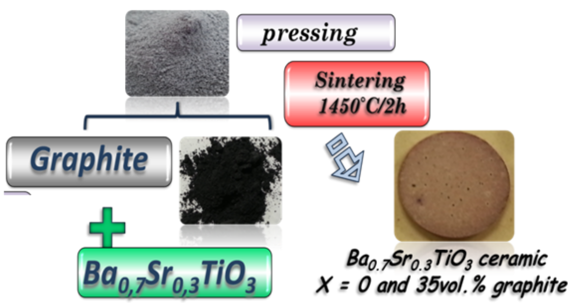
- collaboration with ISTEC-CNR Faenza, Italy
Dr. R. Stanculescu, DFM group, Faculty of Physics, UAIC

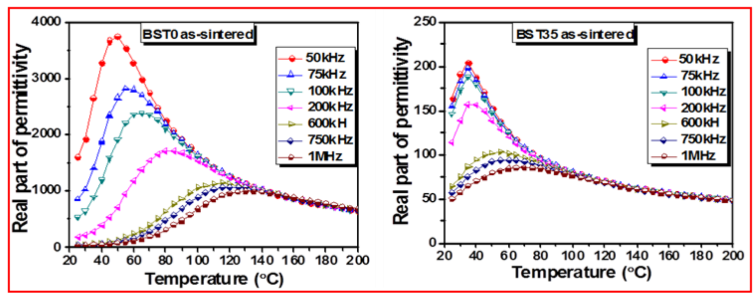
➢ Ferroelectrics

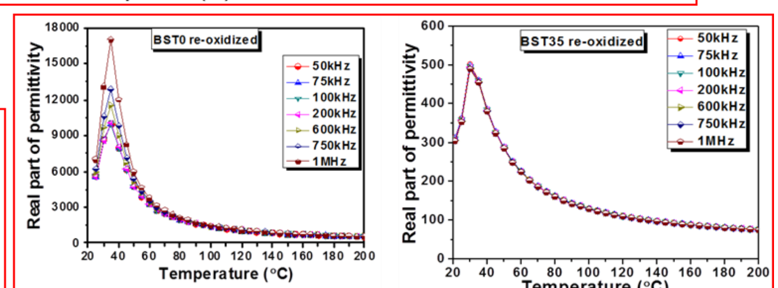
- **The influence of post-sintering re-oxidation treatment on dielectric response of dense and porous $Ba_{0.70}Sr_{0.30}TiO_3$ ceramics**

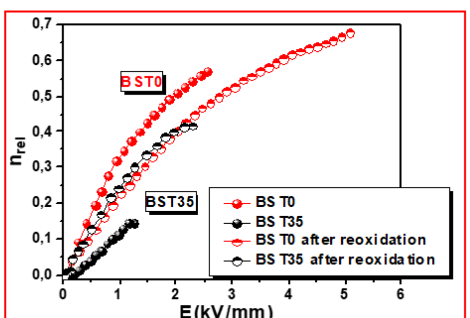












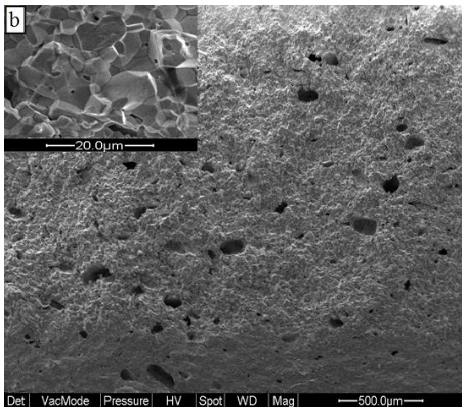
- Stanculescu, RE; Ciomaga, CE et al, The influence of post-sintering re-oxidation treatment on dielectric response of dense and porous Ba0.70Sr0.30TiO3 ceramics Ceram Intl 42,527 (2016)

II. MAIN RESULTS

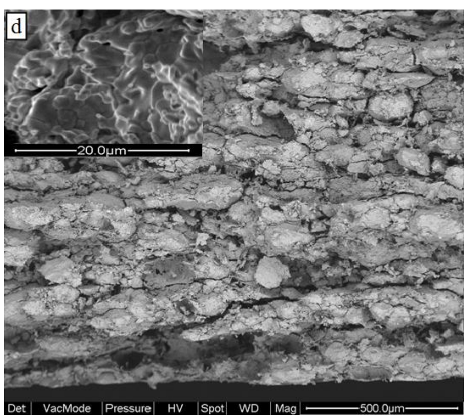
- collaboration with Lect dr. L. Padurariu, DFM group, Faculty of Physics, UAIC

➢ Porous ferroelectric composites

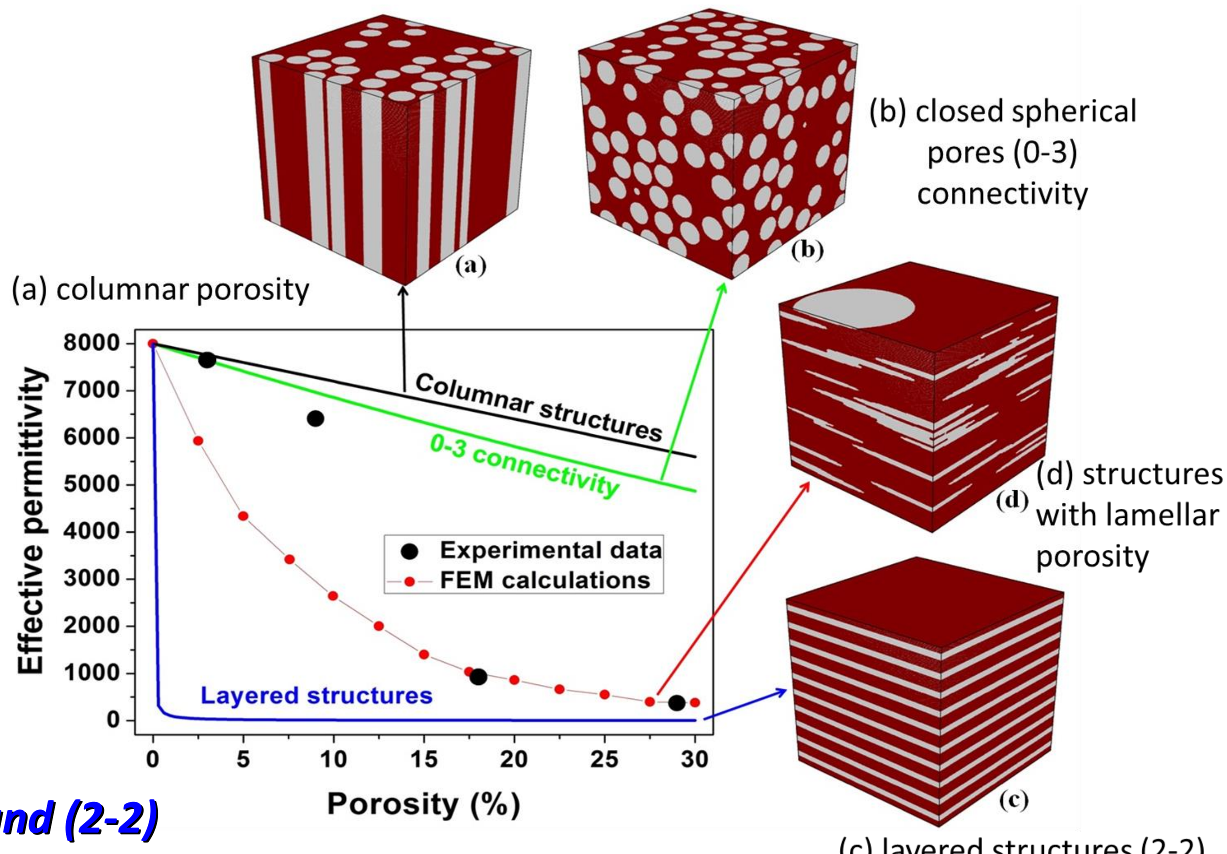
➢ Study of the role of porosity on the functional properties of $Ba_{1-x}Sr_xTiO_3$ ceramics produced by using graphite forming agent



(0-3)



(0-3) and (2-2)



dark - bulk regions, gray - pores

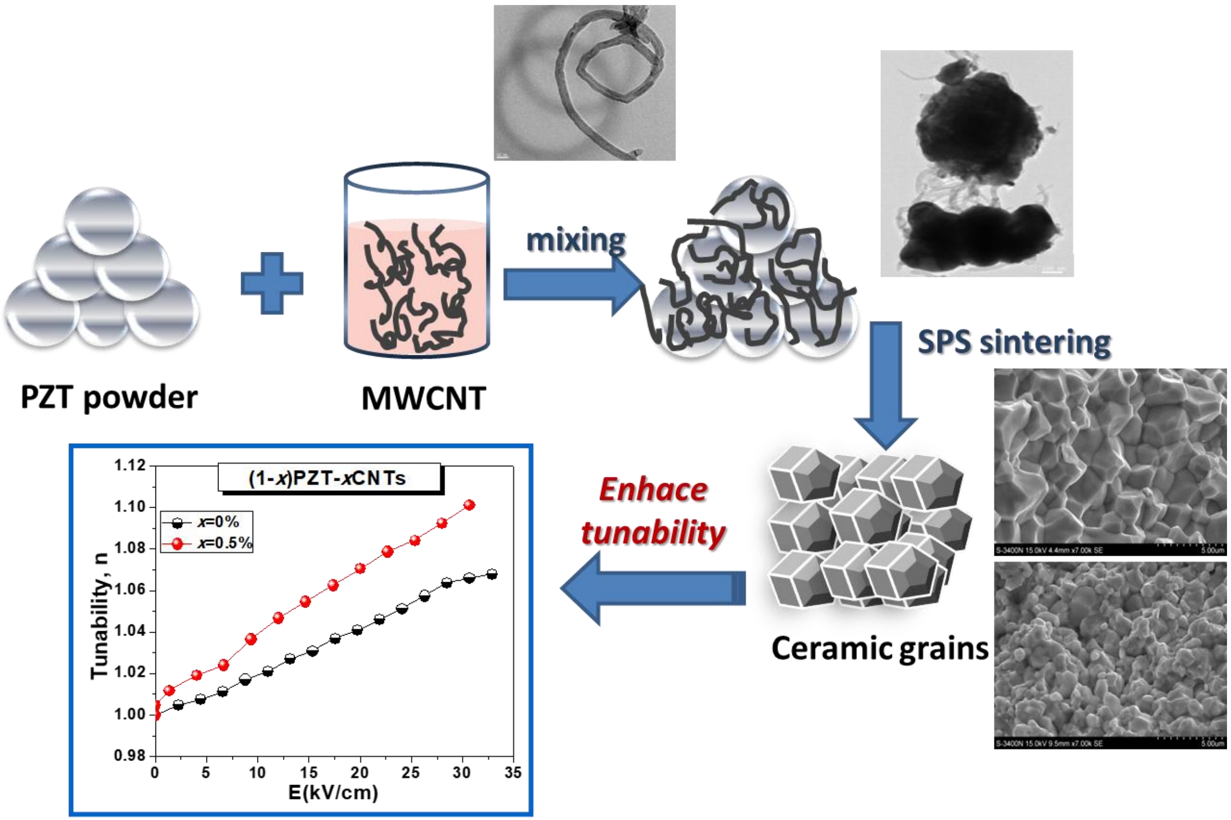
- R. Stanculescu, C. Ciomaga, L. Padurariu et al. **Study of the role of porosity on the functional properties of (Ba,Sr)TiO_3 ceramics**, J . Alloys & Compds. 643, 79 (2015)

II. MAIN RESULTS

- *collaboration with Lect dr. L. Curecheriu, DFM group, Faculty of Physics, UAIC*

➢ Ferroelectric – based composites

• Synthesis and functional properties of $Pb(Zr,Ti)O_3$-CNTs composite, sintered by Spark Plasma Sintering



➢ *by using the MWCNTs in ferroelectric ceramics ⇒ reduce of permittivity with about 14% combined with low losses and higher tunability ⇒ new structures for tunability properties.*

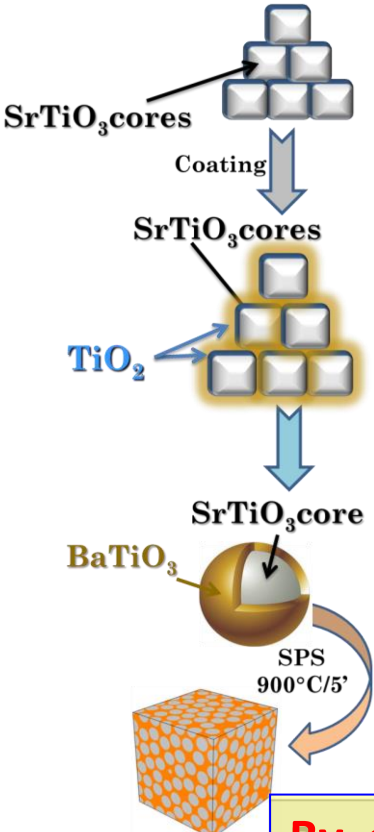
• C.E. Ciomaga, et al, **Using multi-walled carbon nanotubes in spark plasma sintered $Pb(Zr_{0.47}Ti_{0.53})O_3$ ceramics for tailoring dielectric and tunability properties**, Journal of Applied Physics, 116 (16), 164110, (2014).

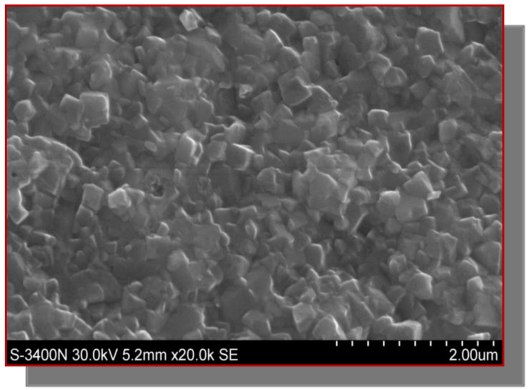
II. MAIN RESULTS

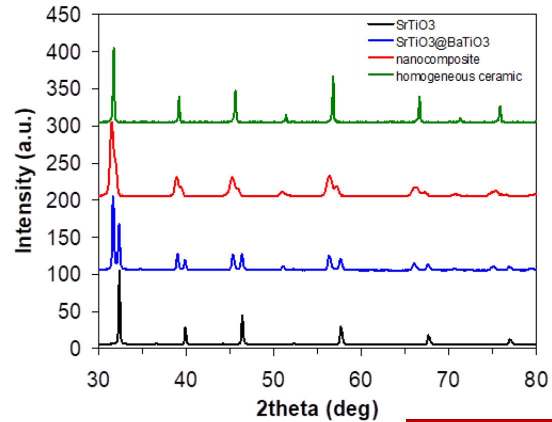
- collaboration with ICMATE-CNR Genoa, Italy
- Lect dr. L. Curecheriu, DFM group, Faculty of Physics, UAIC

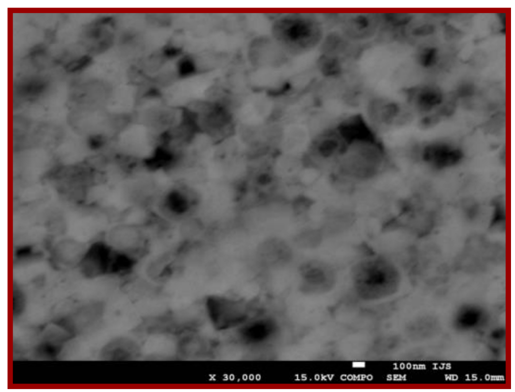
➤ Ferroelectric – based composites

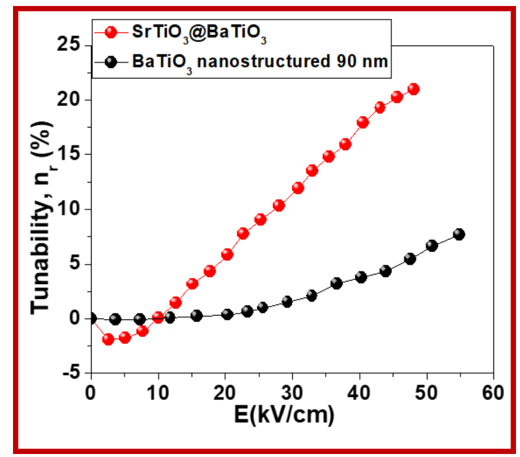
- **Dielectric and non-linear properties of $SrTiO_3$@$BaTiO_3$ core-shell ceramic**











By comparison with the parent phases the $SrTiO_3$@$BaTiO_3$ core-shell ceramic have reduce zero field permittivity and increase the tunability.

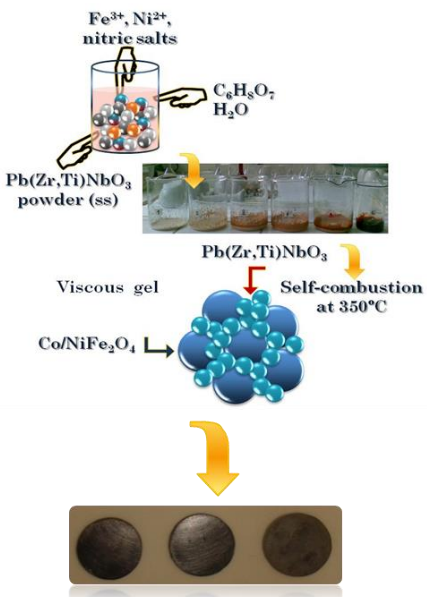
- Airimioaei, M; Buscaglia, MT; Tredici, I; Anselmi-Tamburini, U; Ciomaga, CE et al., $SrTiO_3$-$BaTiO_3$ nanocomposites with temperature independent permittivity and linear tunability fabricated using field-assisted sintering from chemically synthesized powders, J. Mat Chem C 5, 9028 (2017)

II. MAIN RESULTS

- collaboration with Assist.dr. Mirela Airimioaei, Faculty of Chemistry, UAIC

➢ Ferroelectric - magnetic composites

- **$NiFe_2O_4$/$CoFe_2O_4$/$MnFe_2O_4$ with pure and Nb doped $Pb(Zr,Ti)O_3$ ceramic composites**



- C. Ciomaga et al., J. Alloys & Comp. 485 (1-2), (2009) 372-378
- Iordan, AR; Airimioaiei, M; Palamaru, MN; Galassi, C; Sandu, AV; Ciomaga, CE; et al, J. Eur. Ceram. Soc. 29 (13), (2009) 2807
- Ciomaga CE, Scripta Materilia, 62 (8) (2010), 610-612.
- C.E. Ciomaga, et al.J. Appl. Phys. 113, 7, 074103 (2013)
- C.E. Ciomaga et al. J. Eur. Ceram. Soc. 32, 3325–3337, (2012)
- C.E. Ciomaga et al. J. Appl. Phys. 111, 124114 1-6, (2012)
- C. E. Ciomaga, et al. J. Appl. Phys. 112, 094103 1-7 (2012)
- **Patent OSIM** Nr. A/00314 2017, RO-BOPI 11/2018
- **Patent OSIM** Nr. A/00422 2017, RO-BOPI 12/2018

❑ **Grant PN-II-RU-TE 187** *Investigation of the volum, interface and percolation effects in multifunctional composite materials and metamaterials with controlled geometry* (IMECOMP) (2010-2013)

❑ **PostDoctoral grant POSDRU/89/1.5/S/63663** *Studiul ceramicelor nanocompozite cu proprietati electromagnetice emergente - metamateriale. Cercetare si comunicare stiintifica. Popularizarea stiintifica: indicele de refractie negativ si invizibilitate electromagnetica (Proiectarea pelerinei magice a lui Harry Potter?* (2010-2013)

- **$BaTiO_3$-$CoFe_2O_4$/$Co_{0.8}Zn_{0.2}Fe_2O_4$ ceramic composites with different connectivity (0-3, 2-2) by SPS**

- collaboration with IFT, Iasi

- A. Guzu, C. E. Ciomaga et al, J. Alloy.&Compound 796 (2019) 55-64
- C.E. Ciomaga et al., Ceramics International 45 (2019) 24168–24175
- C.E. Ciomaga et al., Journal of Alloys and Compounds 775 (2019) 90-99

❑ **Grant PN-II-PT-PCCA-2013-4-1119** - *Magnetoelectric composites with emergent properties for wireless and sensing applications (2014-2016)*

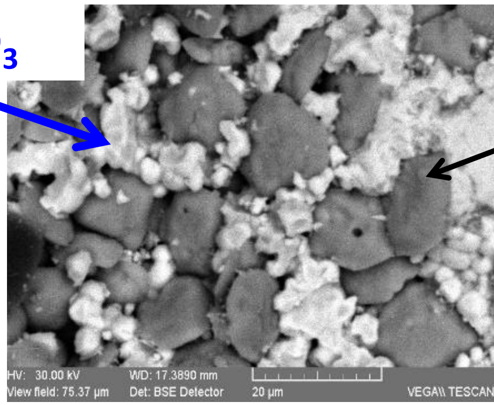
II. MAIN RESULTS

➢ Ferroelectric - magnetic composites

• Double-resonant permittivity and permeability in GHz range: A route towards isotropic metamaterials

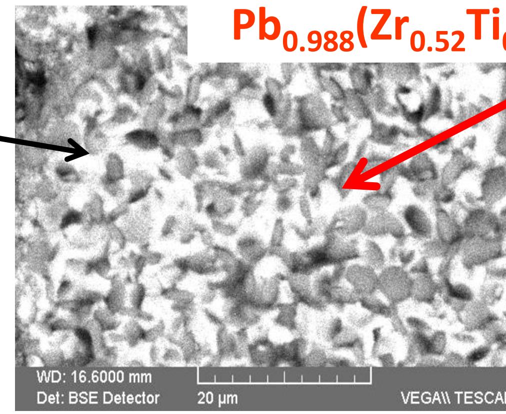
*x*CF-(1-*x*)PZT/PZTNb ceramic composites

$PbZr_{0.47}Ti_{0.53}O_3$

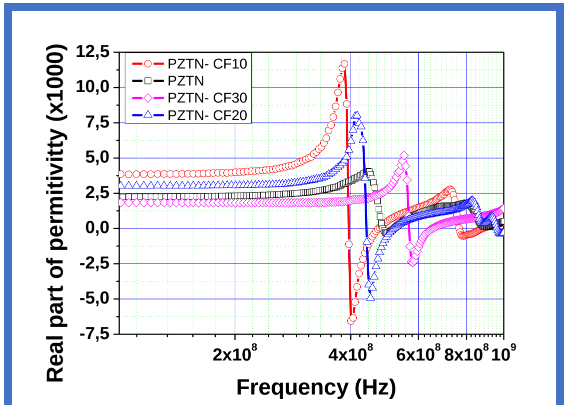


$CoFe_2O_4$

$Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$

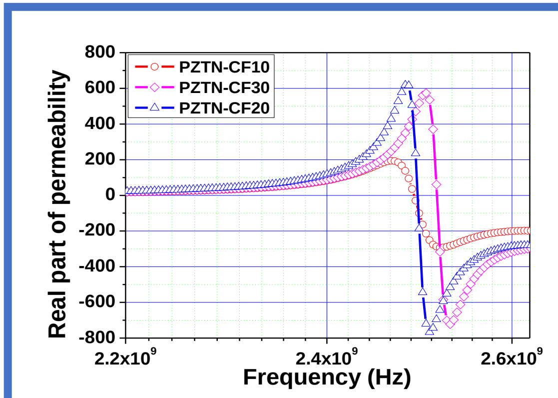


$\varepsilon_r(f) < 0$ and/or $\varepsilon_r(f) < 0$ in the range $4\text{x}10^8 – 2.6\text{x}10^9$ Hz



$$\varepsilon_r = \mu_r$$

for f=280 MHz



• Ciomaga CE, Scripta Materilia, 62 (8): 610-612 (2010).

II. MAIN RESULTS

❑ Project PN-II-RU-TE-2010-0187

Investigation of the volum, interface and percolation effects in multifunctional composite materials and metamaterials with controlled geometry (IMECOMP) (2010-2013)

AIM	Fundamental physics & chemical phenomena related to the volume/interface effects, interconnectivity and percolation degree in ceramic composites and metamaterials with quasi-periodical structure, with dielectric, ferroelectric and magnetolectric properties.

- ✓ **Producing di-phase ME composites**
- ✓ **Investigation of functional (electric, magnetic and magnetoelectric) properties in relation with microstructures**
- ✓ **Implementation of effective fields theories for describing dielectric prop. for different types of microstructures**

Reported results:

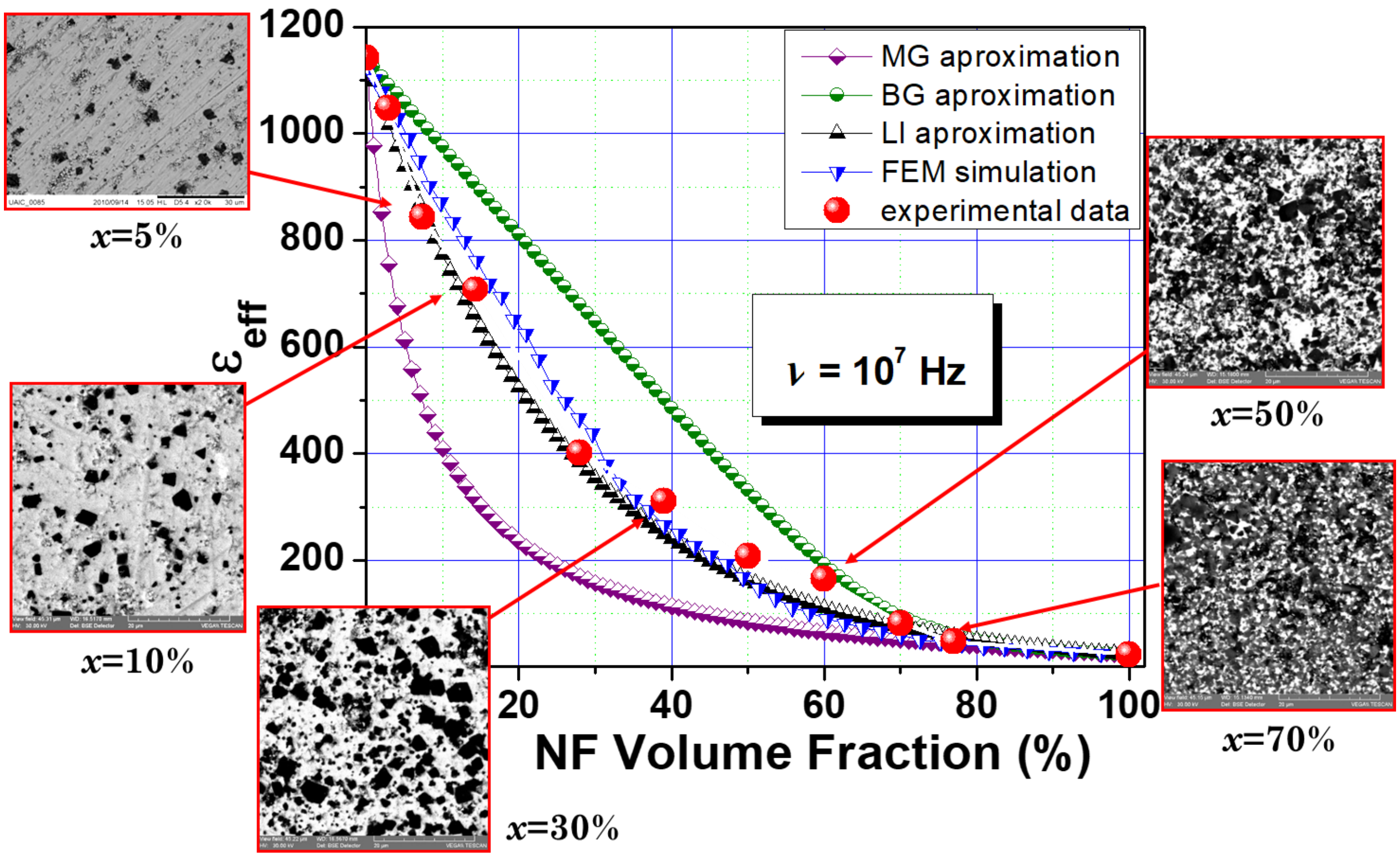
- 8 ISI papers
- 68 scientific presentations to national/international conferences

II. MAIN RESULTS

➢ Ferroelectric - magnetic composites

- **Experimental and analytical modeling in microwave range**

xNF-(1-x)PZTNb ceramic composites



• Ciomaga C.E. et al, *Preparation and magnetoelectric properties of NiFe2O4-PZT composites obtained in-situ by gel-combustion method*, J. Eur. Ceram. Soc. 32, 3325–3337 (2012)

• C.E. Ciomaga, C.S. Olariu, L. Padurariu, A.V. Sandu, C. Galassi and L. Mitoseriu, *Low field permittivity of ferroelectric-ferrite ceramic composites. Experiment and modeling,* J. Appl. Phys. 112, 094103 1-7 (2012).

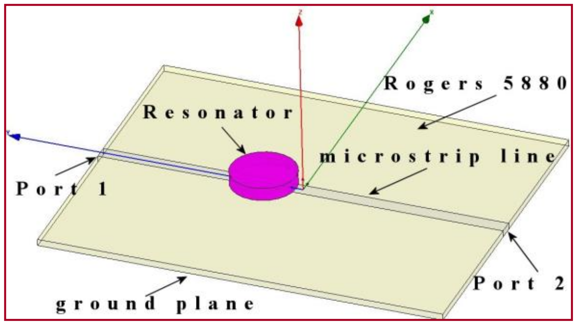
II. MAIN RESULTS

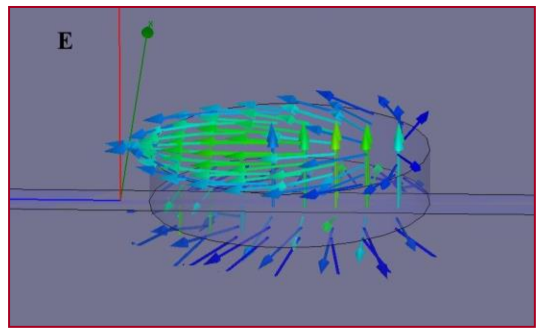
- *collaboration with Lect dr. O. Avadanei, Faculty of Physics, UAIC*

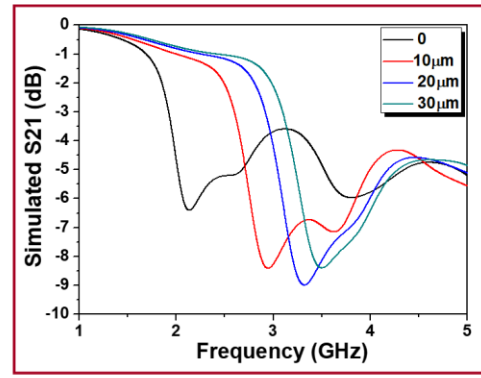
➢ Ferroelectric - magnetic composites

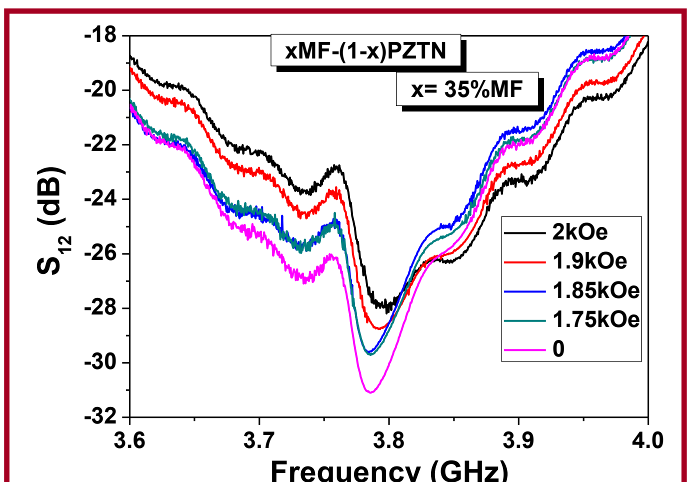
• Engineering magnetoelectric composites towards application as tunable microwave filter

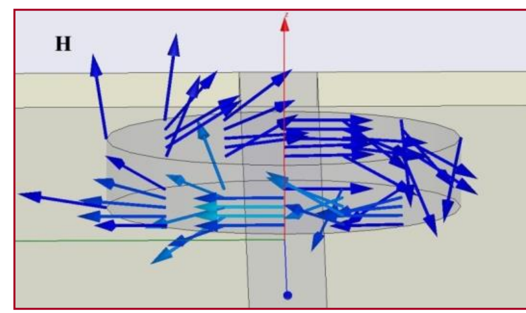
- xMF +(1-x)PZTNb ceramic composites











HEMme$_{11\delta}$ mode field configuration

- Ciomaga, C.E. et al., J.Phys.D: Appl Phys 49 (2016)

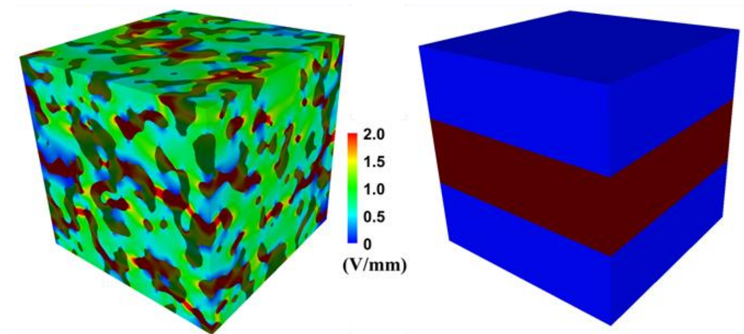
II. MAIN RESULTS

- *collaboration with Lect dr. L. Padurariu, DFM group, Faculty of Physics, UAIC*

➢ Ferroelectric - magnetic composites

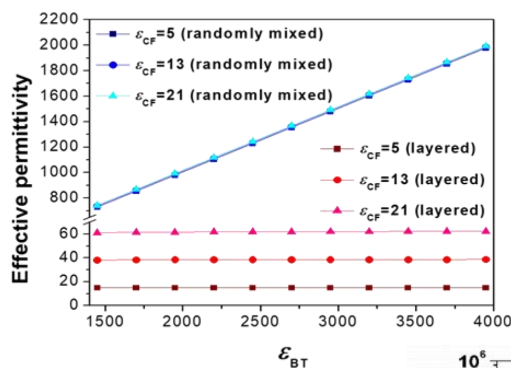
- **$0.66BaTiO_3$-$0.33CoFe_2O_4$ (BT-CF) randomly mixed and layered composites**

Theoretical prediction by FEM

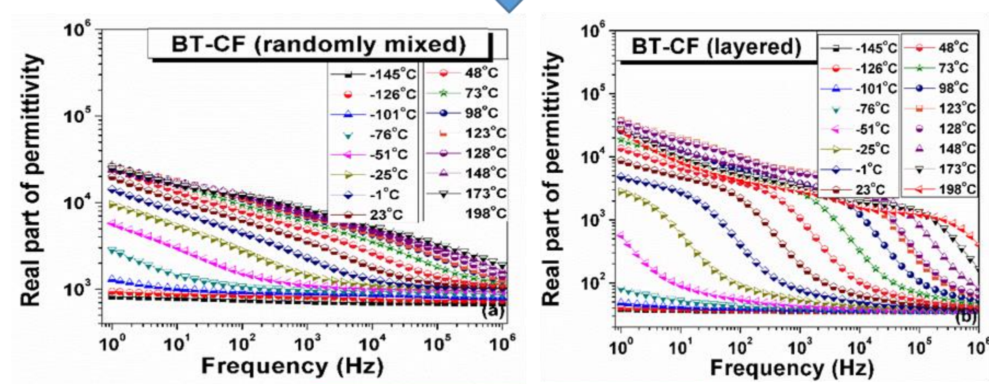


Rondomly mixed BT-ferrite composite

Layered BT-ferrite composite



➢ Finite Element Method (FEM) was used in order to explain the electric field distribution inside the composite materials with different phase connectivity.



Experimental results

• A. Guzu, C. E. Ciomaga, et.al, ***Functional properties of randomly mixed and layered $BaTiO_3$-$CoFe_2O_4$ ceramic composites close to the percolation limit***, J. Alloy.&Compound 796 (2019) 55-64

III. Conclusions

- Contribution to understanding the **effect of compositions, grain size and boundary – dependent phenomena on dielectric properties**; structural phase transitions as well as ferroelectric – relaxor crossover using Landau theory and FORC method

- Oxygen vacancy play an important role on dielectric response in ferroelectric ceramics.

- FEM demonstrated the concept of **engineered local fields in porous microstructures** for tailoring the permittivity and tunability values and the possibility to increase tunability with reducing permittivity for small porosity levels.

- Understanding of the **functional (dielectric, ferroelectric, magnetic and magnetoelectric) related to the structural, microstructural characteristics** in multiferroic composite systems formed by ferroelectric oxide and a spinel ferrite.

- The results obtain by 3D FEM have revealed that there are major differences in the electric field configurations in the randomly mixed and layer microstructure composite, and this demonstrates that **the microstructure and phase connectivity play a major role on the effective dielectric response**.

Perspectives

New porous

Engineering Pb-free porous piezoelectric materials with particular microstructure with enhanced Figure of Merits(FOMs) for energy harvesting applications

- **Grant PN-III-P4-ID-PCE-2020-1988, title *Engineering of lead-free porous ceramic materials for piezo-, pyroelectric sensors with energy harvesting applications (2021-2023)***

- *to design by modelling tools various types of porous ceramic microstructures with enhanced piezoelectric and pyroelectric properties and reduced permittivity with respect to the dense structures*
- *to produce optimised Pb-free porous ceramics with peculiar microstructures*
- *to develop and test piezoelectric and pyroelectric sensors for thermal and mechanical energy detection and conversion in order to be employed in energy harvester devices.*

Perspectives

MPB

Exploring the morphotropic phase boundary (MPB) in ferroelectric systems in order to find high-performance materials with excellent dielectric properties for energy storage applications.

- Using of innovative synthesis technique for obtaining optimum structures with enhanced properties as: high permittivity, tunability, energy storage/conversion/harvesting capacity for advanced applications.

New ferroel

Exploring electrica properties in new classes of ferroelectrics (A_2WO_6 $A=Ln^{3+}$, Bi^{3+})

PN-III-P3-3.1-PM-RO-FR-2019-0069, "Multiscale investigations and modeling of novel ferroelectric oxides NOVOXFER" (dir. L. Mitoseriu) (2019-2021)

Flexible material

Polimer (PVDF, biopolymer) - based composites ($BaTiO_3$, Ferrite, CNT, metallic nanoparticles)

Collaborations: What can I do

DIELECTRICS FERROELECTRICS & MULTIFERROICS GROUP

❑ Synthesis of nanoparticles, ceramics and polymer films by s.s. reactions.

- Chemical niche

- Analytical balance Ohaus (DV215CDV)

- Sand bath

- Calcination furnace 1300^{0}C (Nabertherm L5/13/P330) si 1600^{0}C (Nabertherm LHT04/16/P310),

- Centrifuge 320

- Isostatic press

❑ Broadband impedance spectroscopy (10μHz-3GHz), dielectric measurements and interpretation.

Bridge GWT (20 Hz-10 MHz)

E4991A RF Impedance/Material Analyzer
Frequency range: 1 MHz to 3 GHz

Solartron 1260A Impedance/Gain-Phase Analyzer
Frequency range 10μHz - 32MHz

Directional antenna up to 6GHz

https://eeris.eu/ERIF-2000-000Z-0736

Collaborations: What can I do

DIELECTRICS FERROELECTRICS & MULTIFERROICS GROUP

❑ Piezoelectric measurements

Piezoelectric Tests d33

❑ Ferroelectric measurements: P(E), S(E), FORC, Rayleigh analysis and calculations

Precision Multiferroic II 500V Ferroelectric Test System

❑ Magnetoelectric measurements

- Polarization Measurement under AC & DC Magnetic Fields

- High Voltage Interface
- Bulk Ceramic Heated Piezo/Pyro Test Fixture to 230C
- High Voltage Amplifier 10kV
- Magnetoelectric Test Bundle for Bulk Ceramics
- Thin Film Piezoelectric Test Bundle (TF-PTB)

❑ Non-linear dielectric properties: tunability ε(E)

and (in collab with Lect. Dr. L. Curecheriu);

Trek amplifyer Model 30/20A-H-CE
maximum voltage DC ±30kV @ ±20mA

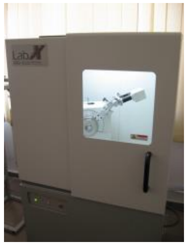
https://eeris.eu/ERIF-2000-000Z-0736

❖ Access structural analysis (XRD)

http://stoner.phys.uaic.ro/major_facilities.html

❑ Expertise on structural analysis by XRD (Shimadzu Lab 6000);

- **Powder and bulk** samples measurements
- **Thin films** samples measurements by grazing incidence method

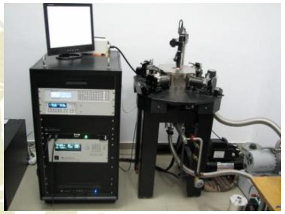


❖ Collaborations on magnetic analysis

SQUID Magnetometer MPMS - XL - 7AC
Maximum field: 7T with integrated AC-coil
Temperature range: 1.9K to 400K
7 Tesla AC Measurements

Dual AGM / VSM Magnetometer

❑ Magnetic characterization (M(H), M(T), FORC analysis by SQUID and AGM);



LakeShore Probe Station with vertical magnetic field

❖ Collaboration in design and predicted of functional properties in various types microstructures by modelling tools

❑ Modeling of the functional properties of composites by *Effective Field Models* and *Finite Element Method* (collab. with Lect. dr. L. Padurariu)

❑ Data interpretation by a complete preparation-micro/nanostructural -functional properties – modeling approach;

Collaborations: I look to share

- **domain structure analysis (AFM, SEM/EBSD) and ferroelectric local switching experiments (PFM)**

- **TEM-SAED and HRTEM analysis**

- **XPS analysis for investigate the reduction of $V_{\ddot{O}}$ and analyse the change of the content of $V_{\ddot{O}}$ in $BaTiO_3$-solid solutions (e.g. $(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_3$ etc)**

- **Exchange of knowledge concerning structural analysis (*Rietveld refinement*)**

- **Ferroelectric oxide materials with dielectric/ferroelectric properties**

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Lecturer

Dr. Mirela Airimioaei
Assistent Teaching

Conf. Dr. Ioan Dumitru

Lector Dr. P. Postolache

Dr. Nadejda Horchidan
Researcher

Dr. Vlad A. Lukacs
Researcher

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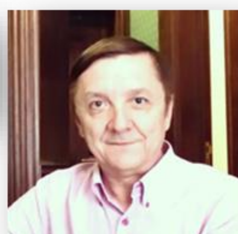

Conf. Dr. Florin Tufescu

RAMTECH
Research Center on Advanced Materials & Technologies

CS II Dr. Sorin Tascu
Researcher

CSIII Dr. Felicia Gheorghiu
Researcher

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Thank you for your attention!