RESEARCH
ALEXANDRU IOAN CUZA UNIVERSITY OF IAŞI

RAMTECH
Research Center on Advanced Materials & Technologies

Investigation of the functional properties of ferroelectric/multiferroic systems

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DIELECTRICS FERROELECTRICS & MULTIFERROICS GROUP

Outlook

1. Introduction

2. Electrical characterisation of $BiFeO_3$-based multiferroic systems by <u>impedance spectroscopy (IS)</u>

➢Precision LCR Meter

➢Impedance/Gain-Phase Analyzer

3. Preparation of $BiFeO_3$ multiferroic micro/nanostructures

➢**<u>Hydrothermal synthesis</u>**

4. PZT –based multiferroic thin films

➢**<u>RF magnetron Sputtering</u>**

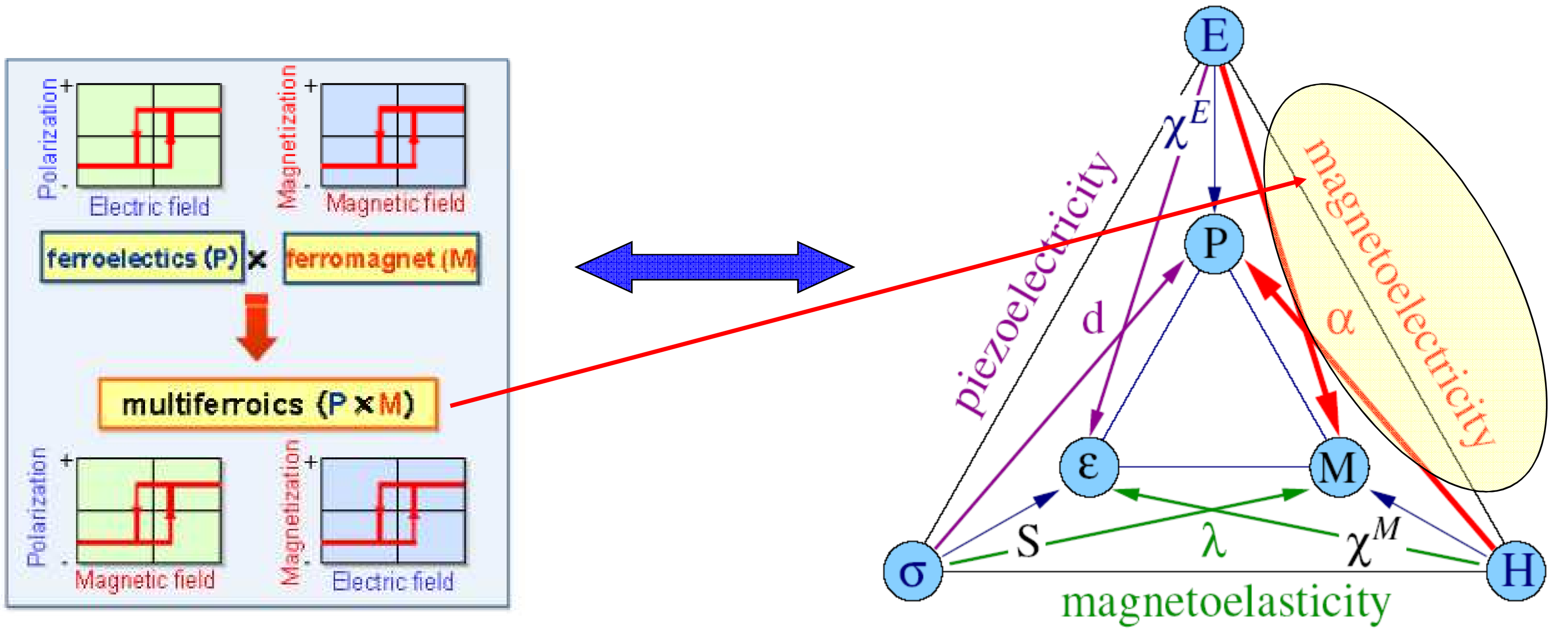
5. Fabrication of PPLN samples

➢**<u> e-field poling method</u>**

Introduction

PhD degree in Physics in 2012 with thesis title "*Study of the electrical and magnetic properties of single phase and composite multiferroic systems*", Supervisor Prof.Dr.Liliana Mitoseriu

- **<u>Magnetoelectrics multiferroics</u>=Co-existance of both ferro/ferri/antiferroelectric and ferro/ferri/antiferromagnetic order in a certain range of temperatures and coupling between them (ME effect).**

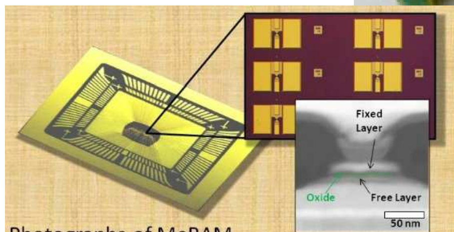


Why multiferroic materials?

Magnetoelectric Multiferroics:

→ **trends in the microelectronic industry:**

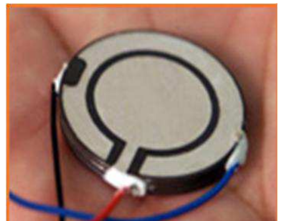
- **Miniaturized components with multifunctional properties**



Photographs of MeRAM memory bits developed by the UCLA team.

Applications:

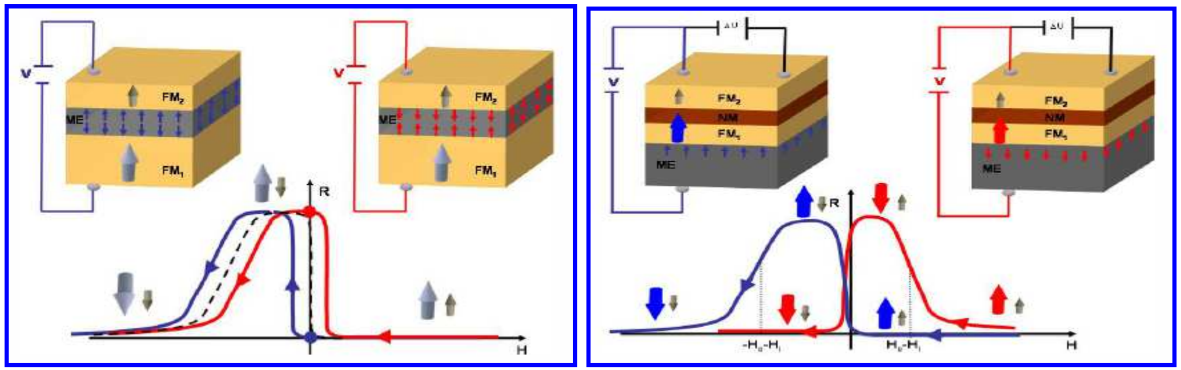
- **ME sensors, transducers, etc.**
- **Multiple state memory elements (writing/reading/deleting with E, H fields and optically)**
- **Spintronics**



Magnetoelectric transformer designed and built at UTA

Requirement:

- **ME materials must exhibit high ME coefficients at room temperature**



- **C. Binek, B. Doudin, "Magnetoelectronics with magnetoelectrics", J. Phys.: Condens. Matter 17, L39–L44 (2005)**

1. Electrical characterisation of $BiFeO_3$-based multiferroic system by impedance spectroscopy (IS)

➢ Precision LCR Meter

Direct measured: R,X,C
Calculated: ε', tgδ, ε", M',M", σ
Frequency: 20Hz – 2MHz

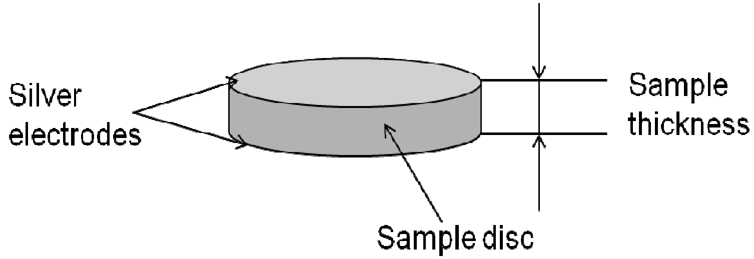
Agilent E4980A Precision LCR Meter controlled via LAN with a computer **(from AMON-CARPHAT Platform)**

➢ Impedance/Gain-Phase Analyzer

Direct measured: ν, ε',ε", σ, R,X,
Calculated: M',M", tgδ
Frequency: 1Hz – 1MHz

Solartron Impedance/Gain-Phase Analyzer model 1260A from the "Dielectrics,Ferroelectrics and Multiferroics" Laboratory of the "Alexandru Ioan Cuza" University

Sample type



➢The electrical measurements were performed on parallel-plate capacitor configuration, by applying Ag electrodes onto the polished surfaces of the sintered ceramic disks with diameters in the range of 9-10 mm and 1- 2 mm thickness.

➢ Precision LCR Meter

Direct measured: R,X,C, L
Calculated: ε', tgδ, ε", M',M", σ,ρ
Frequency: 20Hz – 20MHz

Wayne Kerr 6500P LCR Meter from the RAMTECH Centre of the "Alexandru Ioan Cuza" University

Investigated multiferroic systems

➢ $BiFeO_3$ based single-phase multiferroic systems

Pure $BiFeO_3$ ceramics

$BiFeO_3$-based solid solution

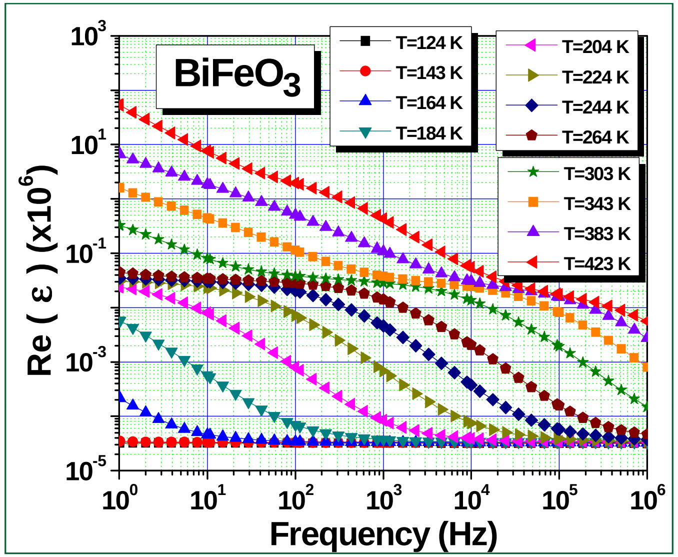
- **$(1\text{-}x)BiFeO_3\text{-}xBaTiO_3$**
- **$BiFe_{1-x}Mn_xO_3$**
- **$Bi_{1-y}La_yFe_{1-x}Mn_xO_3$**

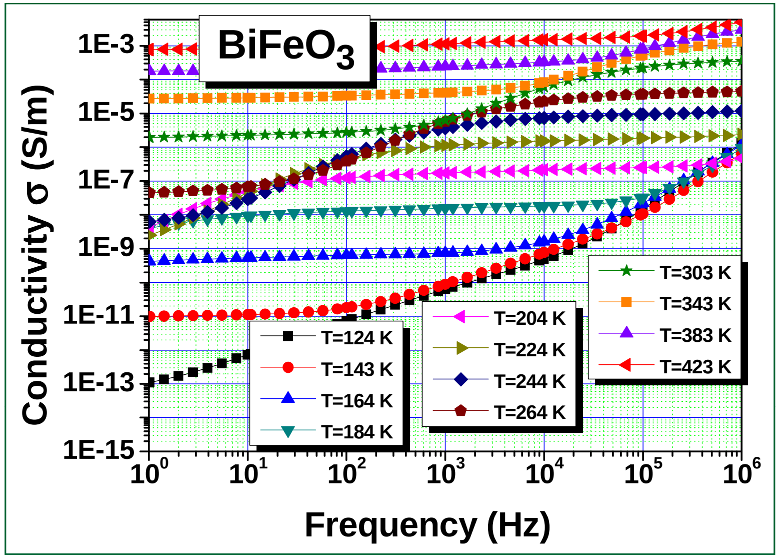
Unsolved problems:

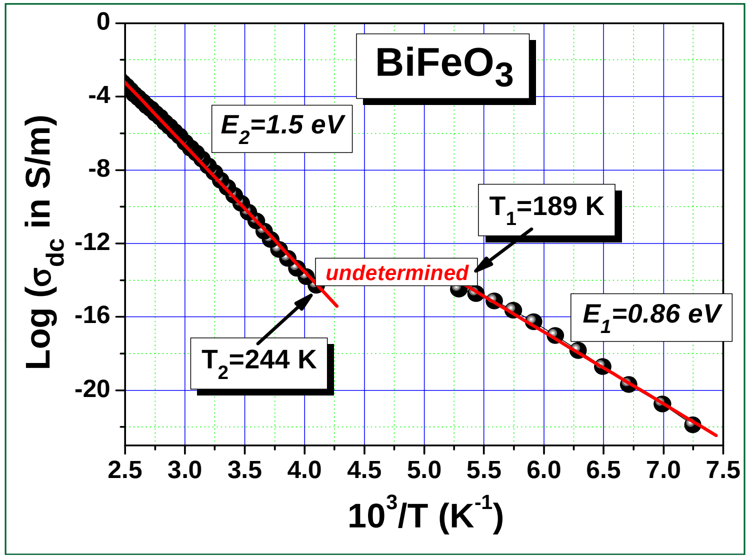
➢ To explain the macroscopic properties in relation with microstructure and composition of the single-phase $BiFeO_3$ compounds

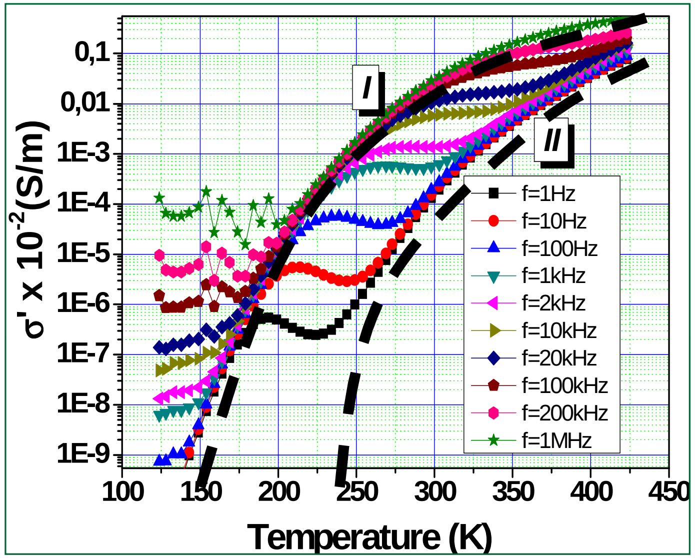
➢ To understand the mechanisms of conduction and dielectric relaxation

Conductivity anomaly









➢a strong reduction with frequency of the ε

➢ two region in conductivity plot :
1) almost constant
2) a large increase,

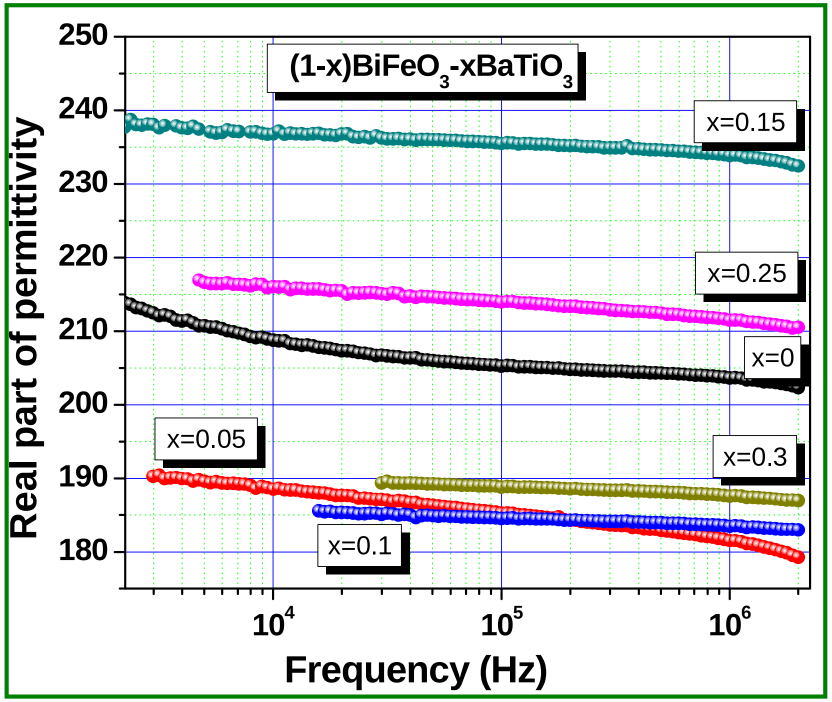
separated by the range of temperature (189 – 244) K

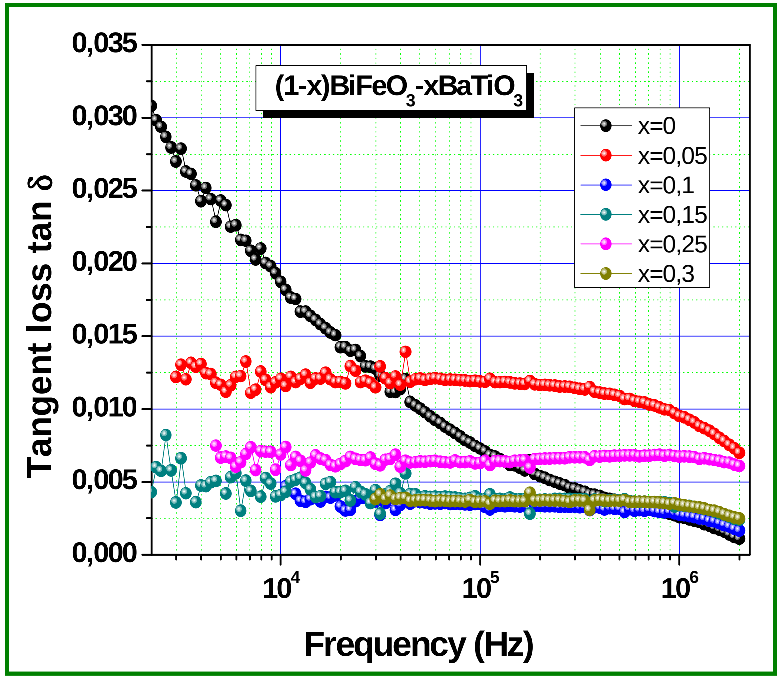
1. Felicia Gheorghiu, Mihai Calugaru, Adelina Ianculescu, Valentina Musteata and Liliana Mitoseriu, Preparation and functional characterization of $BiFeO_3$ ceramics: a comparative study of the dielectric properties , Solid State Sciences, Solid State Sciences 23 (2013) 79-87

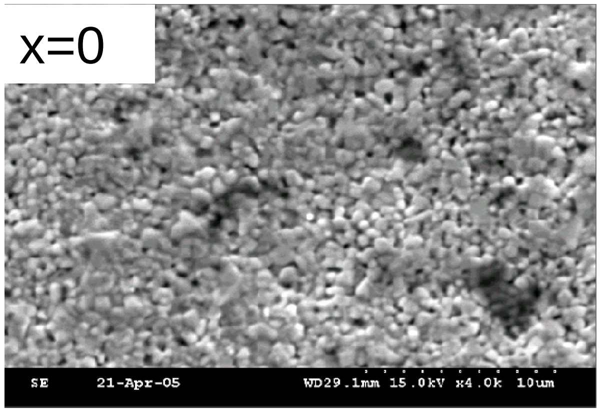
2. Lavinia Curecheriu, Felicia Gheorghiu, Adelina Ianculescu, Liliana Mitoseriu, Non-linear dielectric properties of $BiFeO_3$ ceramics, Appl. Phys. Lett. 99, (2011) 172904

3. Felicia Gheorghiu, Lavinia Curecheriu, Adelina Ianculescu, Mihai Calugaru and Liliana Mitoseriu, Tunable dielectric characteristics of Mn-doped BiFeO3 multiferroic ceramics, Scripta Materialia 68 (2013) 305–308

Dielectric characteristics







⇒ Presence of $BaTiO_3$ in solid solution results in:
- elimination of conduction mechanisms ,
- stabilization ε'=(180-240) and
- reduction of dielectric losses below 3% at room temperature.

1. Felicia Prihor, Adelina Ianculescu, Liliana Mitoseriu, Petronel Postolache, Lavinia Curecheriu, Dragan N. and Crisan D., Functional properties of the (1-x)$BiFeO_3$ – x$BaTiO_3$ solid solutions, Ferroelectrics 391 (2009) 76 – 82
2. Felicia Prihor Gheorghiu, Adelina Ianculescu, Petronel Postolache, Nicoleta Lupu, Marius Dobromir, Dumitru Luca, Liliana Mitoseriu, Preparation and properties of (1-x)$BiFeO_3$ – x$BaTiO_3$ multiferroic ceramics, J. Alloys Compd. 506 (2010) 862–867
3. Adelina Ianculescu, Felicia Prihor Gheorghiu, Petronel Postolache, Ovidiu Oprea, Liliana Mitoseriu, The role of doping on the structural and functional properties of $BiFe_{1-x}Mn_xO_3$ magnetoelectric ceramics, J. Alloys Compd. 504(2010) 420–426

2. Preparation of $BiFeO_3$ micro/nanostructures

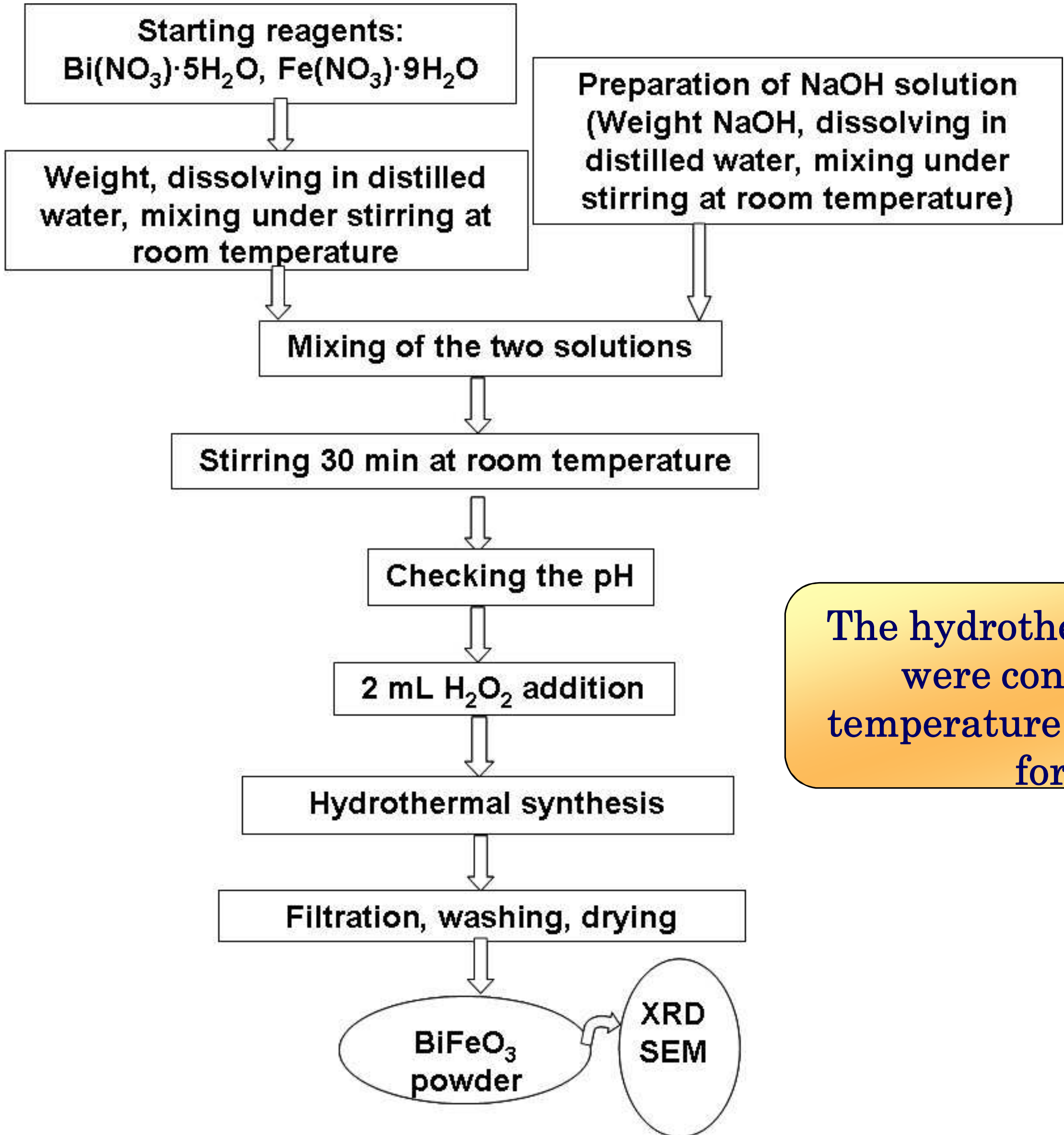
➢ Hydrothermal synthesis

Univ. of Genoa & Institute of Energetics and Interphases
IENI-CNR, Genoa, Italia

Advantages:

⇨ low temperatures (< 200°C);

⇨ reaction takes place in a closed system under a high pressure as an additional parameter (besides temperature, precursors, solution pH, reaction time)

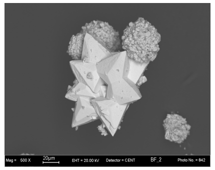
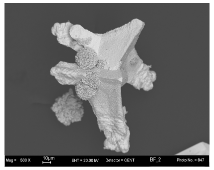
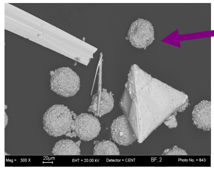


The hydrothermal treatments were conducted in the temperature range 180-220°C for 4-48h.

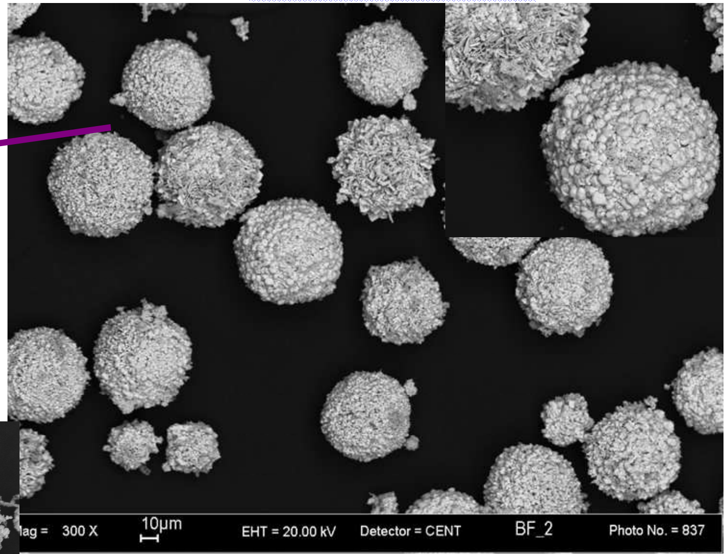
The reaction furnace and hydrothermal vessel

Microstructural characterization

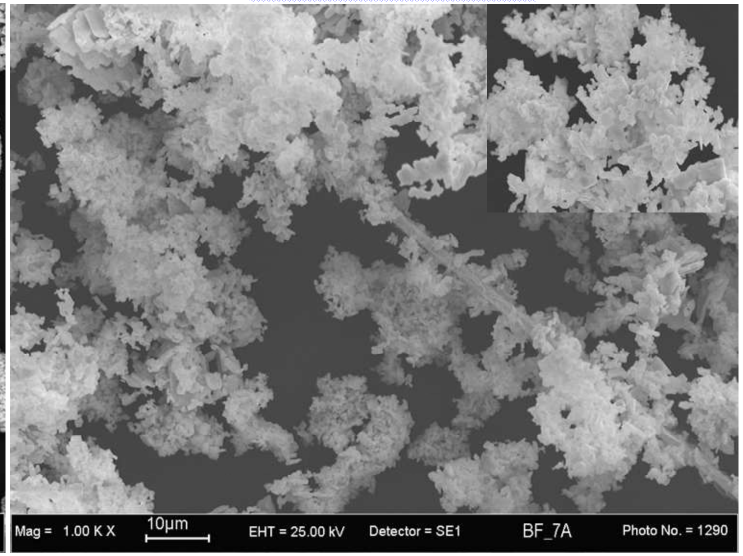
$BiFeO_3$ powders

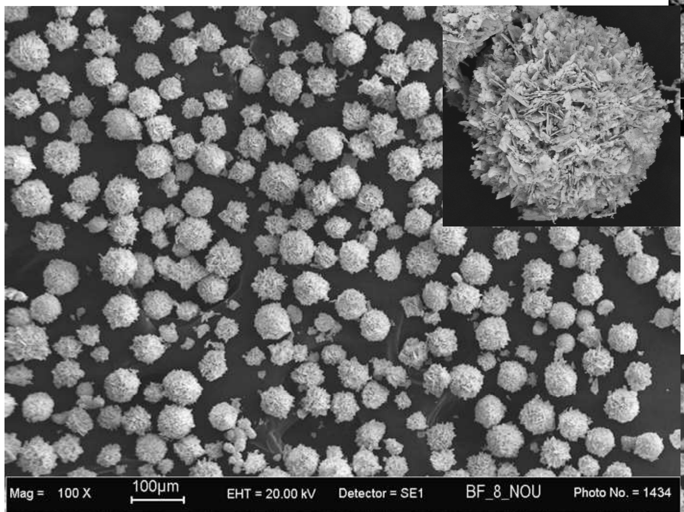
200°C/48h



220°C/48h

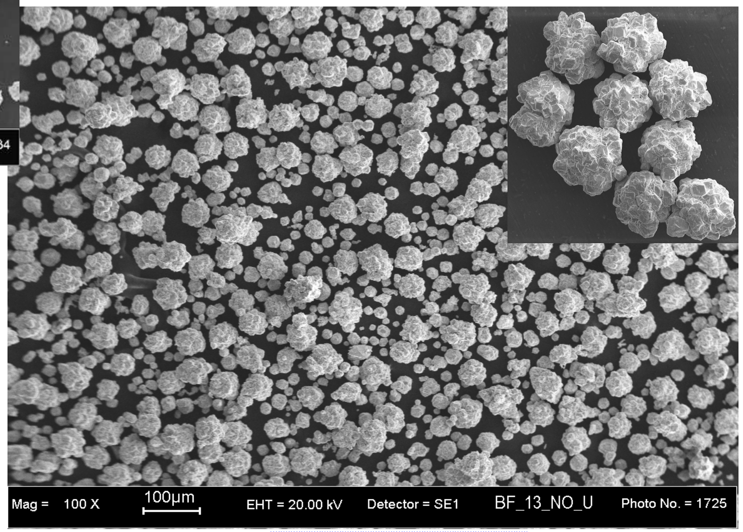


180°C/48h

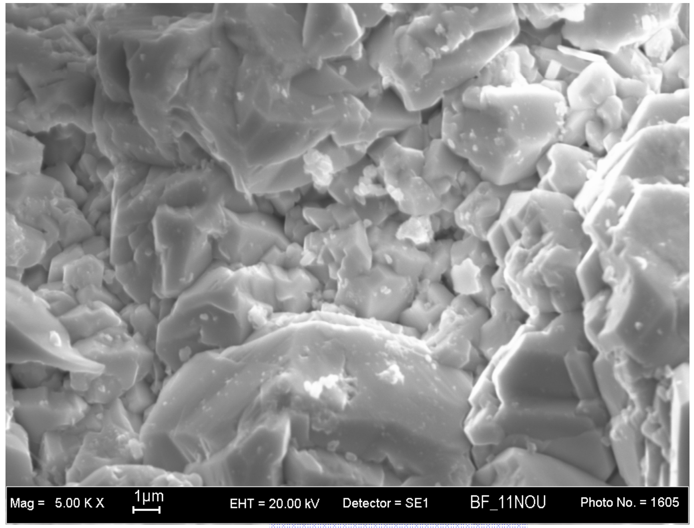


Felicia Gheorghiu*, *Radu Tanasa, Maria Teresa Buscaglia, Vincenzo Buscaglia, Cristina G. Pastravanu, Eveline Popovici and Liliana Mitoseriu, Preparation of $Bi_2Fe_4O_9$ particles by hydrothermal synthesis and functional properties, Phase Transit 86 (7) (2013) 726-736

Optimum conditions:
-180°C reaction temperature,
- 8h reaction time,
- 0.001667 mol/L precursors concentration,
- 1.2 mol/L NaOH concentration.



180°C/8h



180°C/4h

RAMTECH Centre: powders and ceramic preparation

Analytical Balance
GH-252-EC

Ball Milling
Grinding

Hydraulic Press-Carver

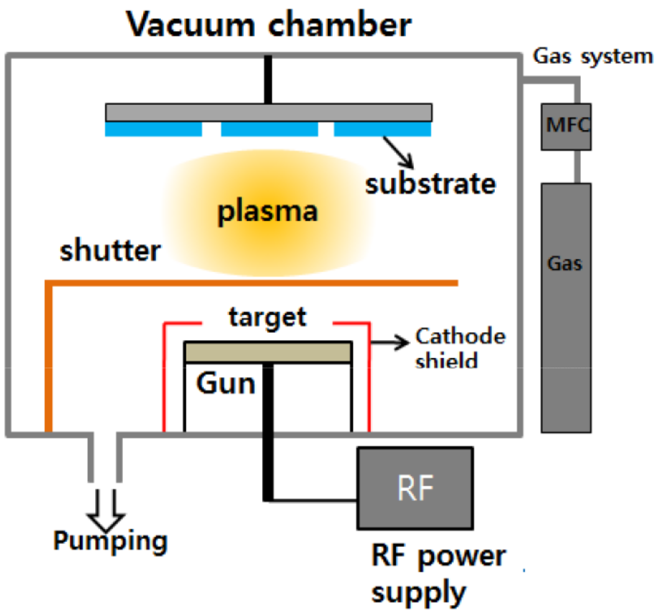
Carbolite Furnace

Auto Precision
Polishing Machine

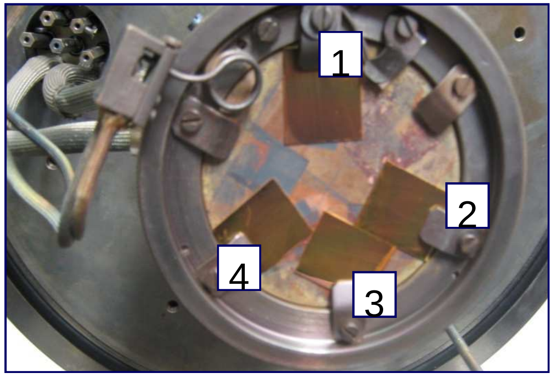
Complex impedance
investigation

3. PZT –based multiferroic thin films

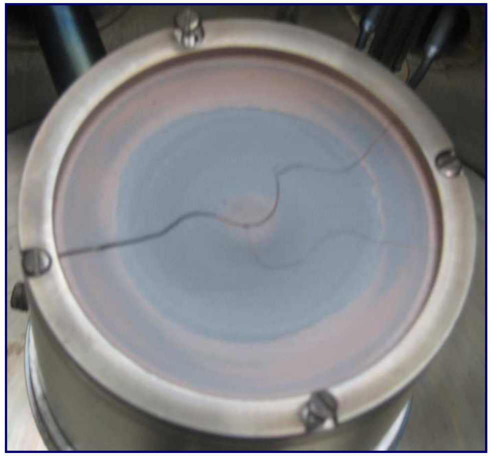
➢RF magnetron Sputtering



Schematic representation of a sputtering system



Substrate positioning

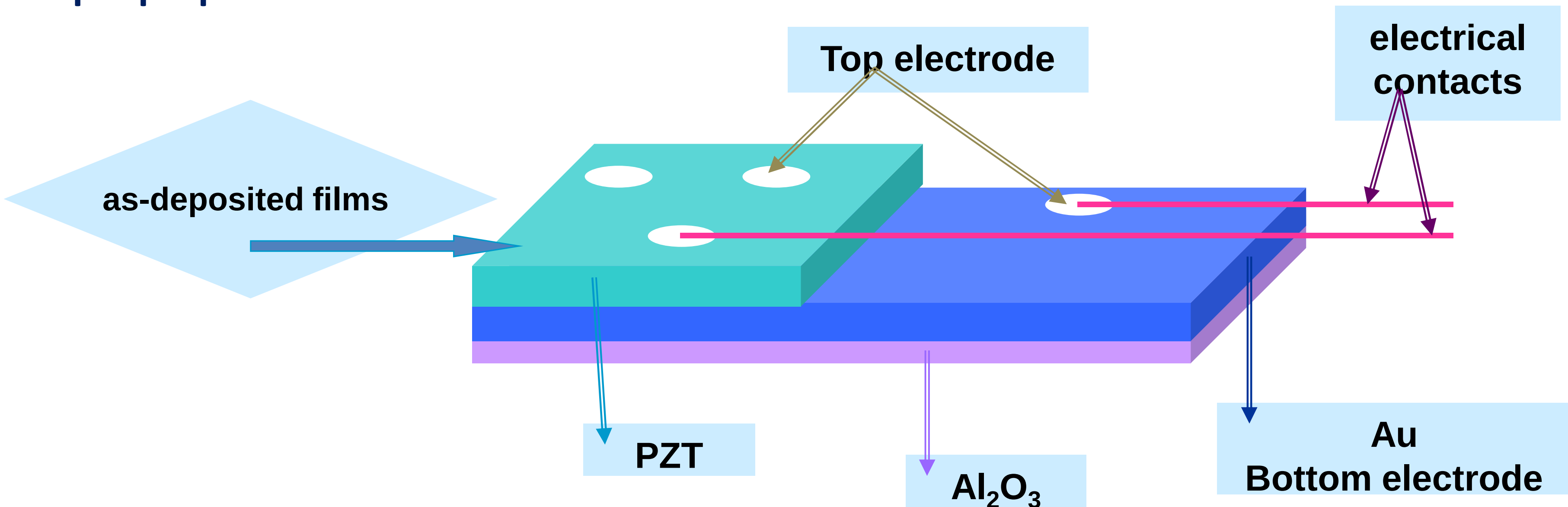


The target after deposition (broken)

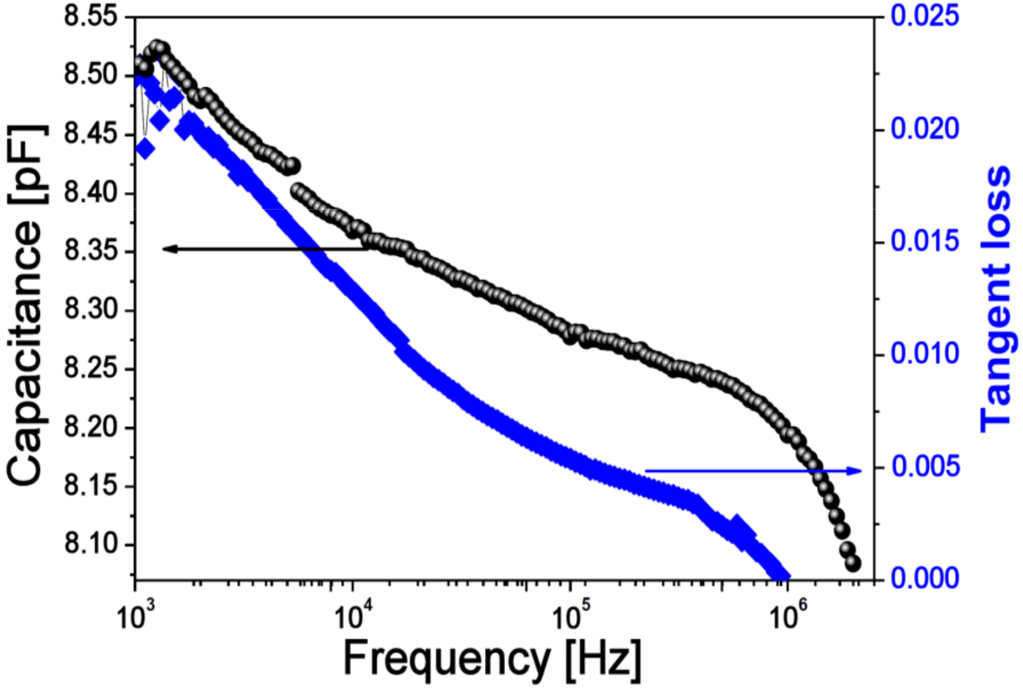
Deposition conditions:

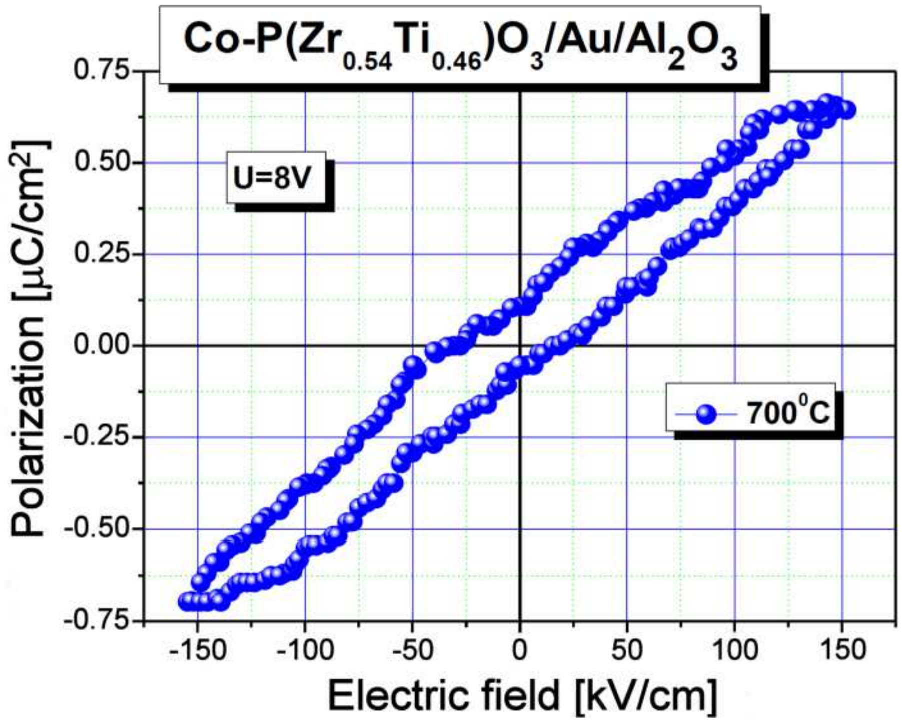
- Ceramic target : Co-doped $Pb(Zr_{0.54}Ti_{0.46})O_3$ (Kurt J. Lesker Company)
- Diameter: 3.00"
- Substrate: Au/Al_2O_3
- Discharge in Ar
- Basic pressure: 2×10^{-6} mbar
- Working pressure: 1.5×10^{-3} mbar
- Substrate temperature: 300°C

Sample preparation for electrical measurements:



Co-doped PZT thin films characterization





Advantages of RF Sputtering:

1. It works well with insulating targets
2. High efficiency: easier to keep plasma going which can operate at lower Ar pressures (1-15 mTorr)

1. Raluca Frunza, Dan Ricinschi, Felicia Gheorghiu, Radu Apetrei, Dumitru Luca, Liliana Mitoseriu, Masanori Okuyama , Preparation and characterisation of PZT films by RF-magnetron sputtering , J. Alloys Compd. 509 (2011) 6242–6246

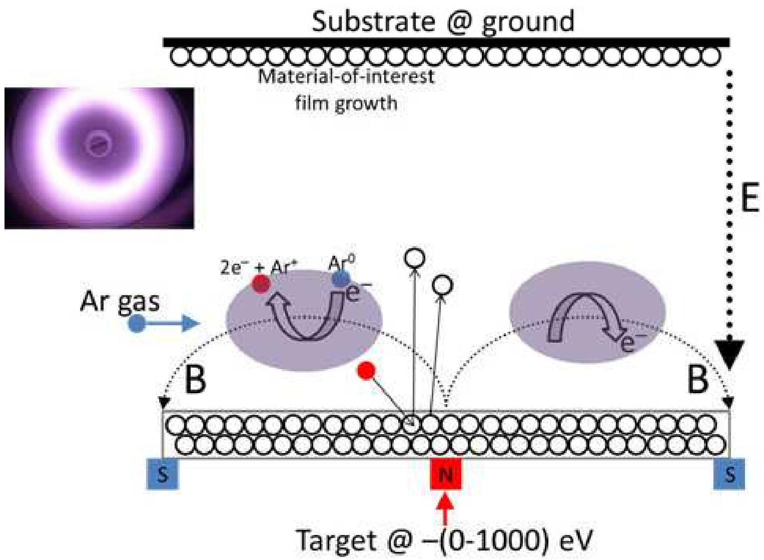
2. Felicia Gheorghiu, Radu Apetrei, Marius Dobromir, Adelina Ianculescu, Dumitru Luca, Liliana Mitoseriu, Investigation of Co-doped PZT films deposited by rf-magnetron sputtering, Processing and Application of Ceramics 8[3] (2014) 113-120

RAMTECH Centre –thin films deposition

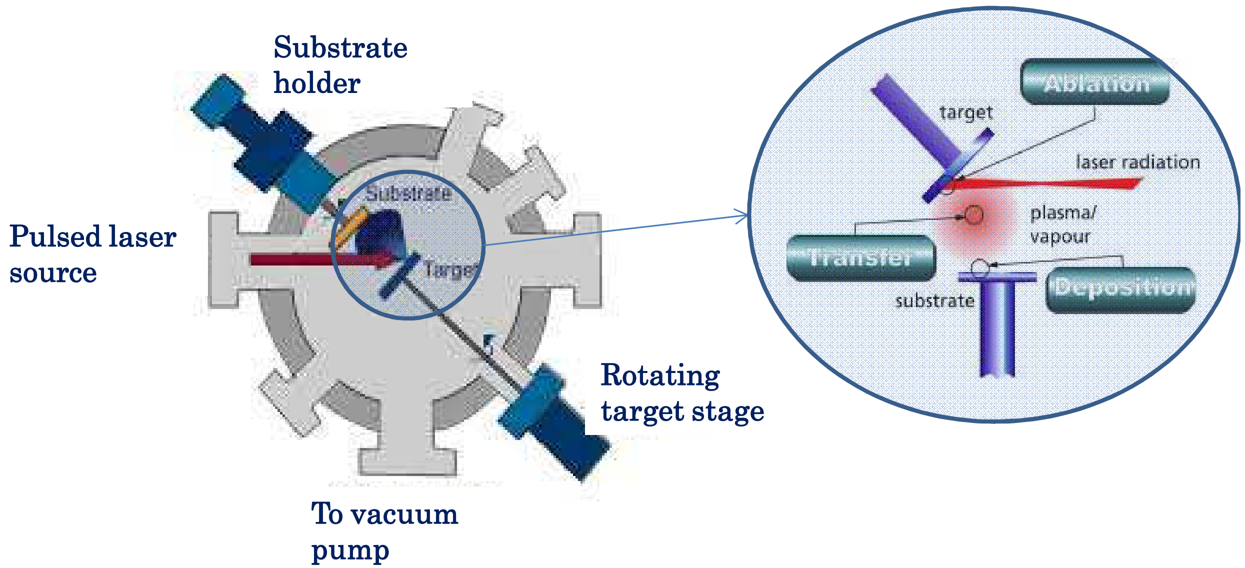
Magnetron sputtering system type Q150T S/E/ES

Pulsed Laser Deposition (PLD) system

Principle

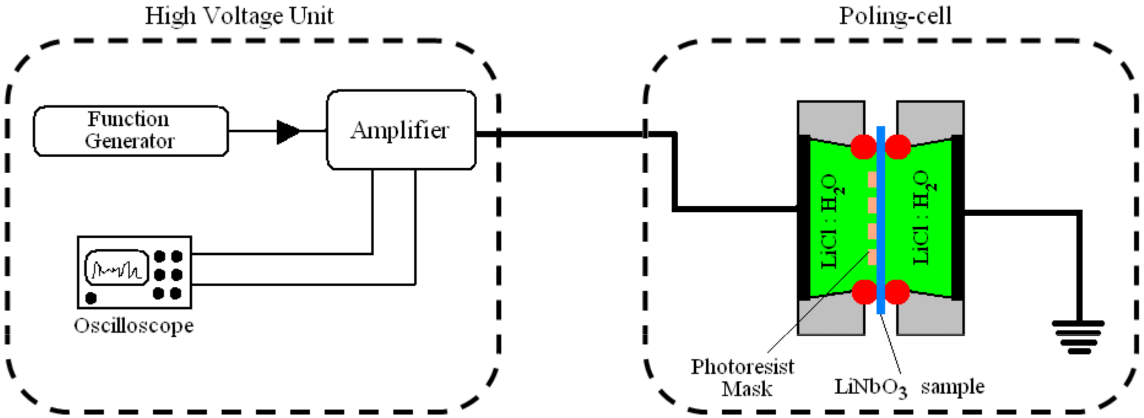


Principle



4. Fabrication of PPLN samples

➢ *e*-field poling method

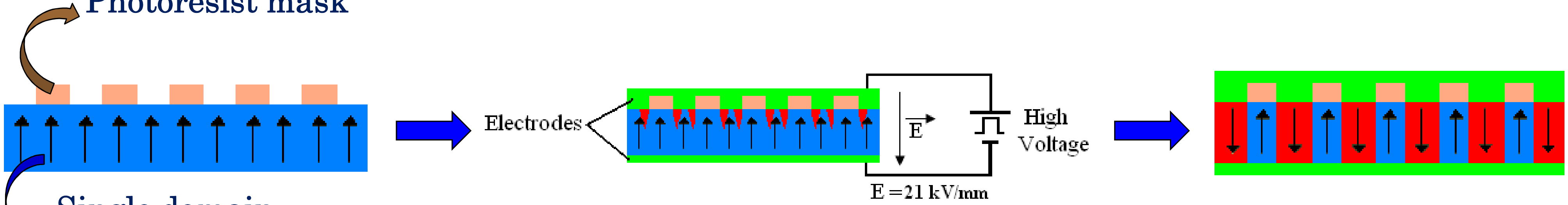


E-field poling setup

PPLN=Periodically Poled $LiNbO_3$

E-field poling method steps:

Photoresist mask



Single domain ferroelectric substrate

Inversion of ferroelectrics domains by application of an electric field

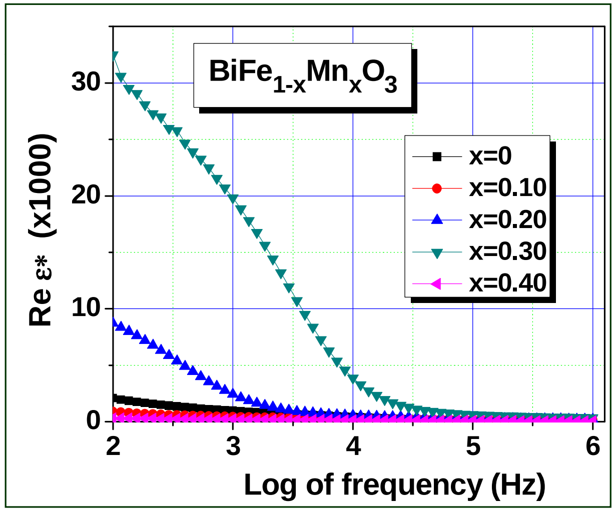
Substrate after removing the external electric field

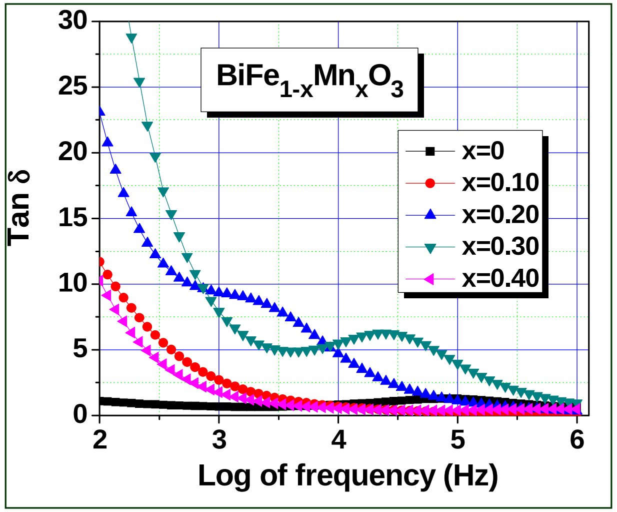
RAMTECH Project PN-II-ID-JRP-2014:
"INtegrated Quantum Circuits based on non-linear waveguide Arrays"

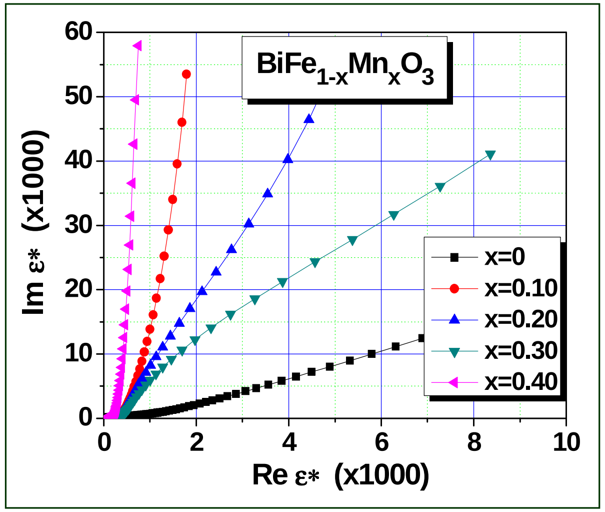
Parteners:
Research Center on Advanced Materials and Technologies (RAMTECH) Sciences Department, "Alexandru Ioan Cuza" University of Iaşi,
Laboratoire de Physique de la Matière Condensée (LPMC), Université de Nice – Sophia Antipolis, Nice, France
Laboratoire de Photonique et Nanostructures (LPN), Centre National de la Recherche Scientifique (CNRS), Paris, France

Conclusions

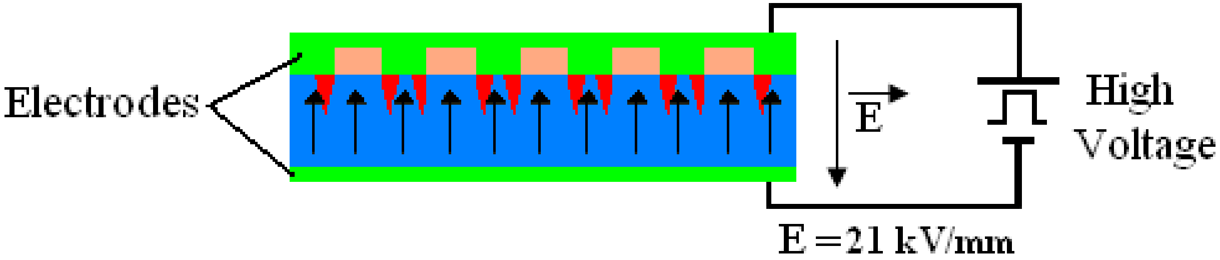
- Electrical characterisation of ceramics by <u>impedance spectroscopy (IS)</u>







- Fabrication of PPLN samples by <u>e-field poling method</u>



Inversion of ferroelectrics domains by application of an electric field

Thank you for your attention!