POLITECNICO DI TORINO

DISAT

Department of Applied Science and Technology

National Research Council of Italy

Institute of Science and Technology for Ceramics

PhD XXIX cycle

PRODUCTION OF MULTIFUCTIONAL CERAMIC COMPOSITES: BULK MATERIALS AND THICK FILMS

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Motivation

- Multifunctional materials

Layout

Introduction: multifunctional composites

Production Technologies

- Conventional Ceramic Process: Solid State Reaction method (SSR)
- Electrophoretic deposition (EPD).

Single phases

- Nb-doped Lead Zirconate Titanate (PZTN).
- Cobalt Ferrite (CFO).
- Titanium dioxide (TO).

Composites

Particulate ceramic composites

- CFO-TO → magneto-dielectric
- CFO-PZTN → magnetoelectric

Laminate ceramic composites

- Bilayer thick film by EPD → CFO-TO/PZTN and CFO/PZTN
- Miniaturized structure by tape casting and screen printing

Multifunctional Ceramic Materials:

Applications

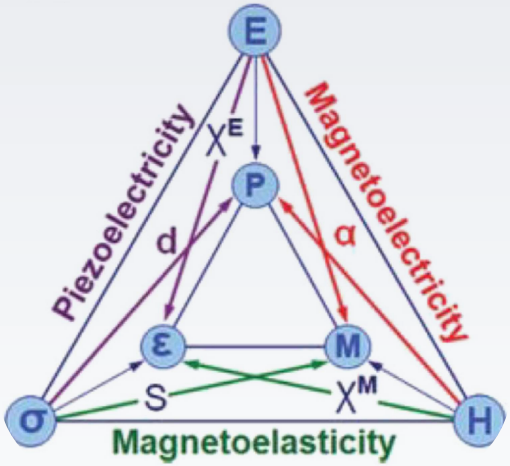
- Data storage
  - Multiple-state logic memories
  - Non-volatile memories
- Wireless telecommunications
  - Tunable devices
  - Resonators
  - Filters
  - Phase shifters and delay lines
  - Miniaturized antennas
  - Terahertz emitters
- Sensors
- Conversion of energies
- Energy harvesting

•Greater perfomances

•Wearable applications

•Miniaturization

Relationship between the order parameters and their mutual coupling coefficients



"All-in-one universal solid state element"

Capable of mechanical actuation, multiple memory states, logic functions, sensing and photoactive properties with unprecedented versatility for high-tech applications.

"... have the potential to fundamentally transform our society and to allow the current scientific and technological progress to continue"

[] M. M. Vopson. Critical Reviews in Solid State and Materials Sciences, 40:223-250, 2015

Why

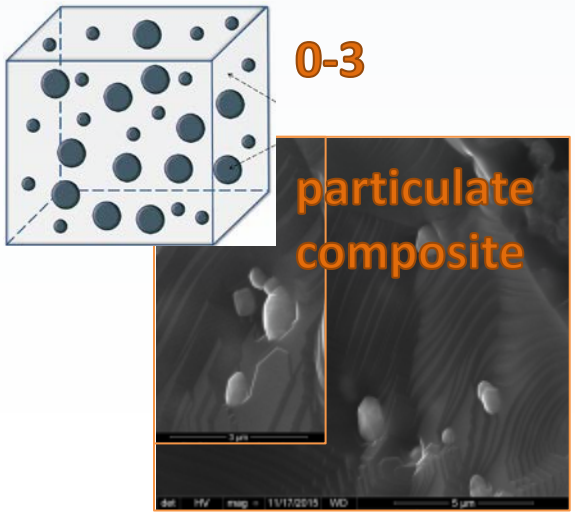
PRODUCTION OF MULTIFUCTIONAL CERAMIC *composites:*

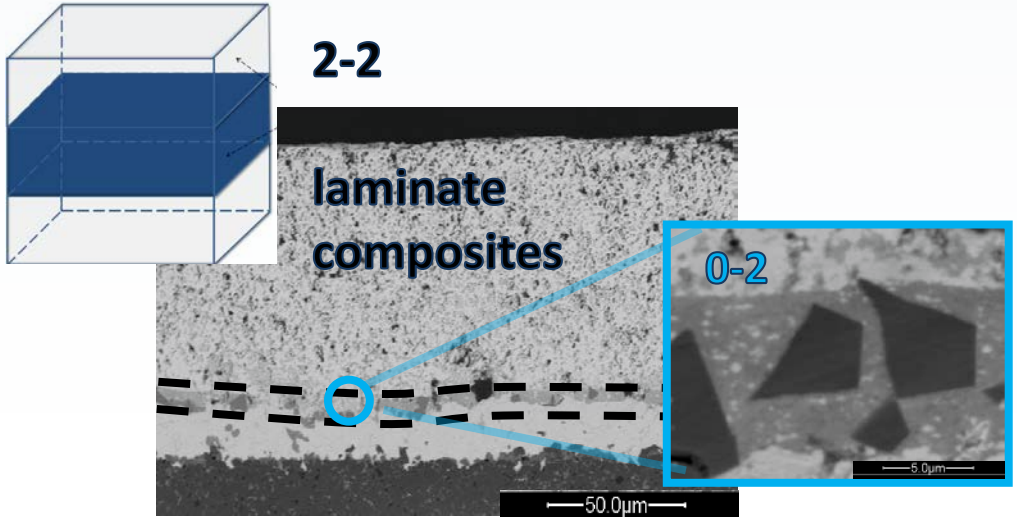
BULK MATERIALS AND THICK FILMS *?*

"An elegant solution to single phase (multifunctional) *dilemma* (weak magneto-electric coupling) *was the developed of* (multifunctional*) composite materials"*

[] M. M. Vopson. Critical Reviews in Solid State and Materials Sciences, 40:223-250, 2015

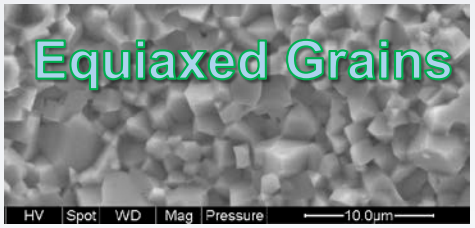
DESIGN AND PREPARATION IN VIEW OF MULTIFUNCTIONALITY

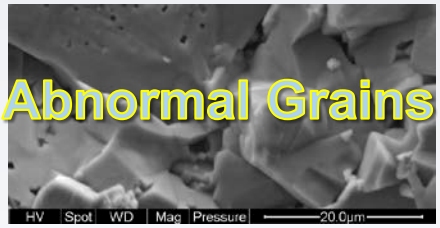


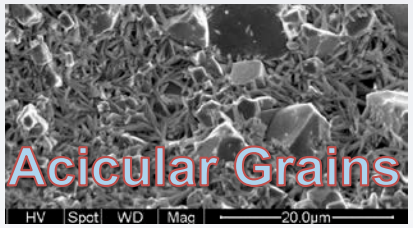


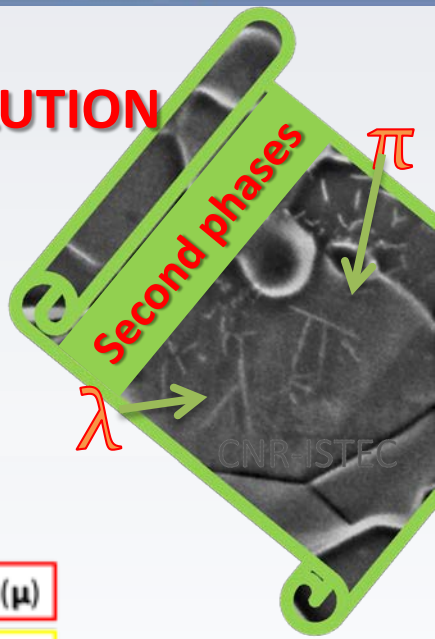
Newnham's composite classification
[] R.E. Newnham, et al. Cross, Mater. Res. Bull. 13, 525 (1978)

PROCESSING RELATED ISSUES IN MICROSTRUCTURE EVOLUTION

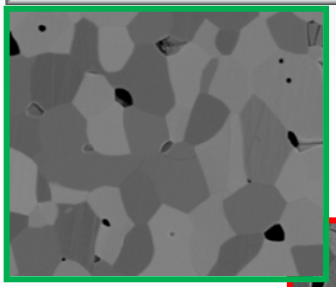




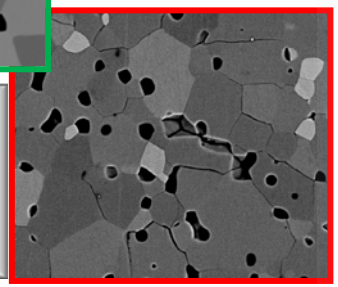


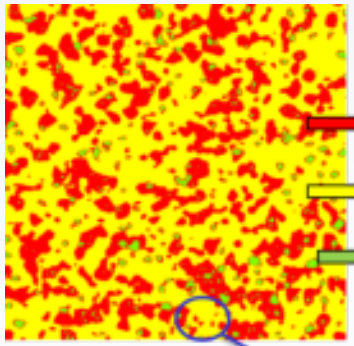


Grain Boundaries Adhesion

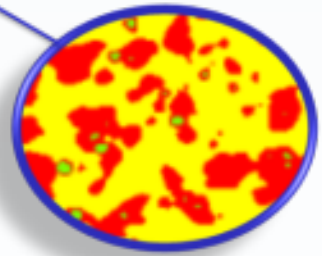


Pores and mechanical defects

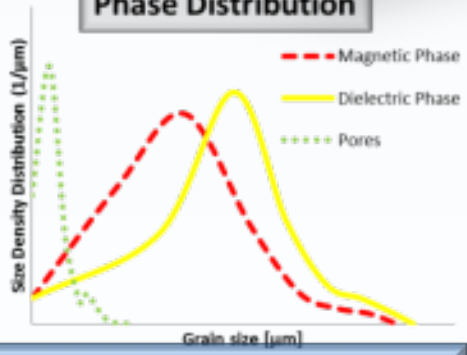




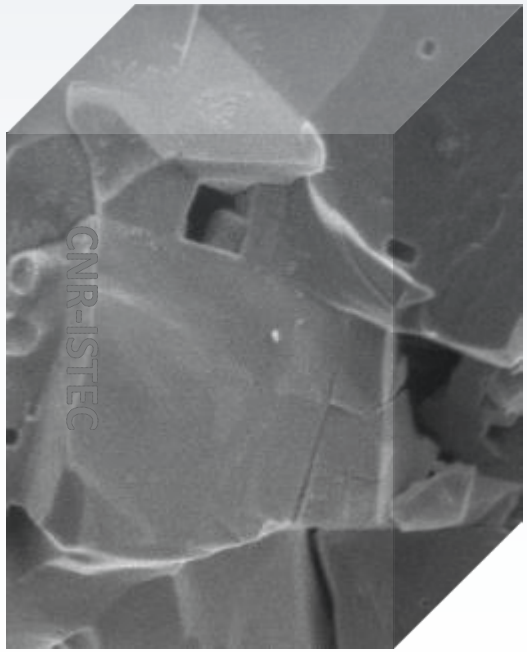
Phase Dispersion



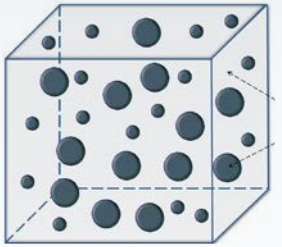
Phase Distribution



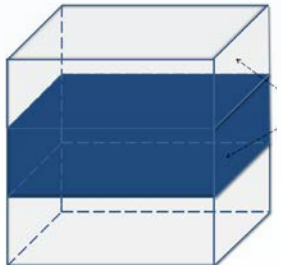
The approach



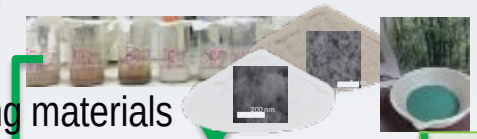
1 to produce ME ceramic composites with 0-3 connectivity by mixing phases produced by SSM



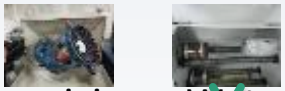
2 to produce ME laminated ceramic structures with 2-2 connectivity by EPD



Typical preparation procedure of a bulk ceramic materials by the SSR method



- Starting materials
- Batching



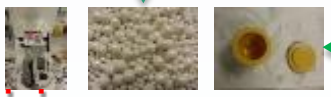
- Mixing

Dry mixing

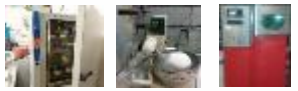
Wet mixing

- Drying
- Sieving

- Calcination



- Milling/mixing



- Drying

Oven

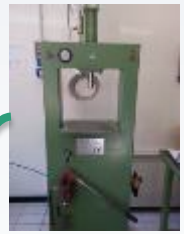
Rotary evaporator

Freeze-drying

- Sieving

P O W D E R S

Shaping

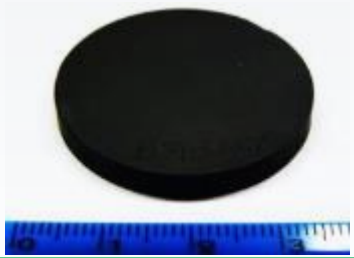


Uniaxial pressing

Isostatic pressing

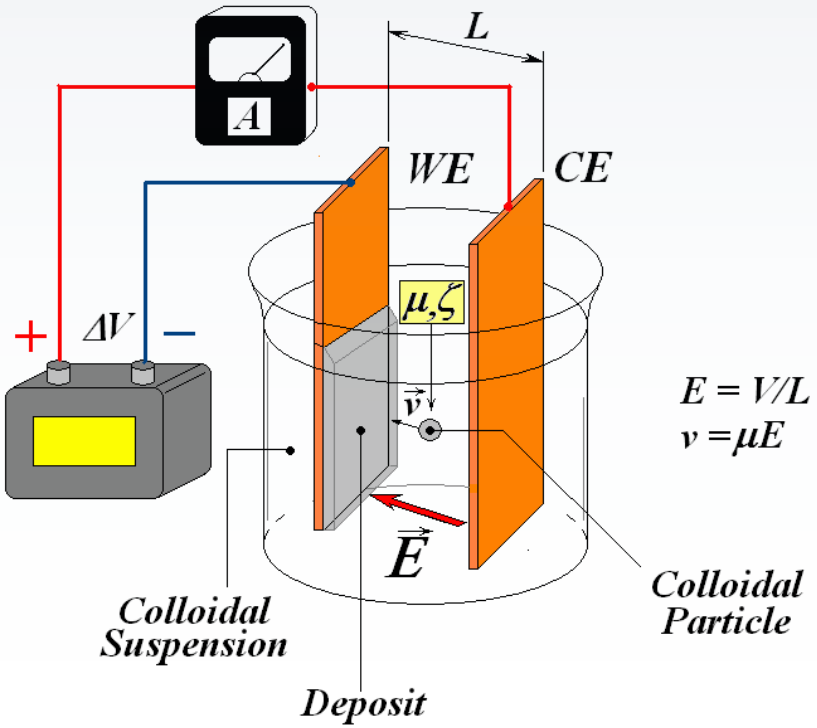
Green body

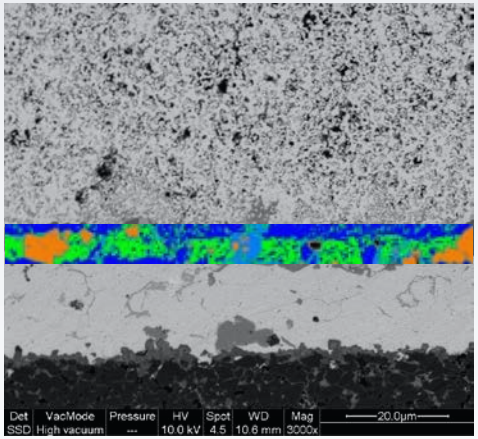
Sintering



Bulk material

Electrophoretic deposition (EPD) was applied to prepare magnetoelectric (ME) composite bilayer thick films based on perovskite phase and spinel cobalt ferrite





Advantages

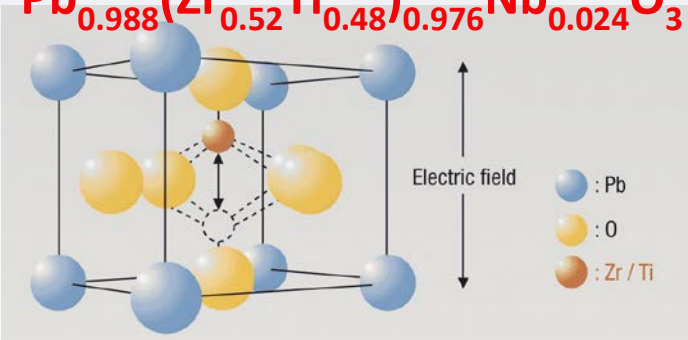
- Simple apparatus
- Short formation time
- Little restriction of the shape substrate
- High degree of stoichiometry
- Debonding is not required

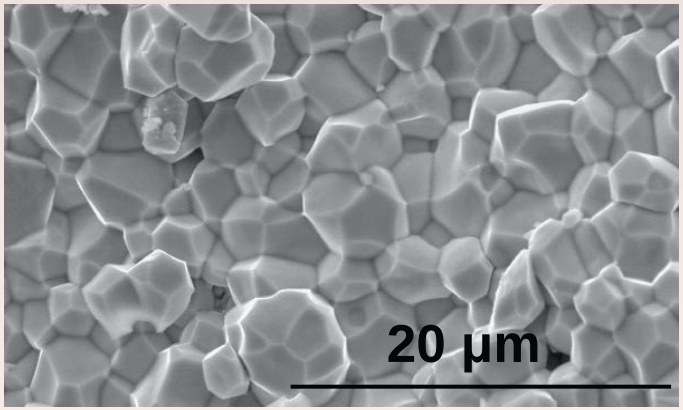
Processing of the single phases

Ferroelectric phase PZT Lead Zirconate Titanate

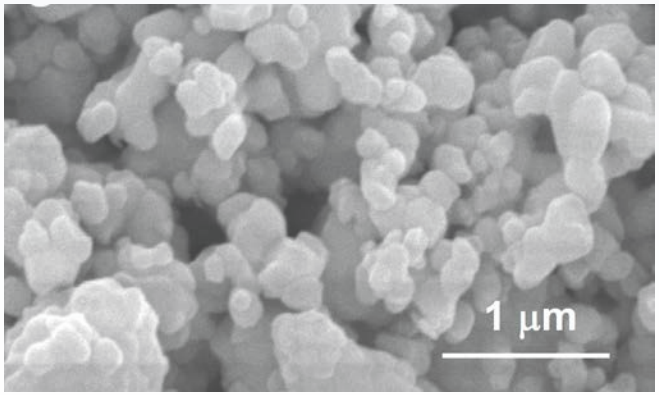
Solid state reaction

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





SSR PZT 1200°C 2h



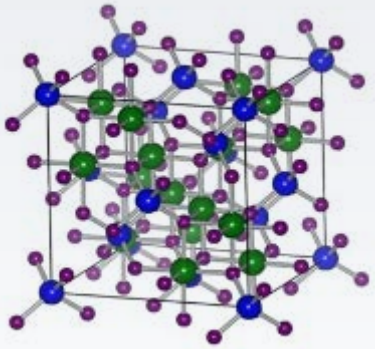
as calcined powders

High electromechanical coupling factor

Synthesis	Sample	ρ %	ε_{33}^T	k_p	k_{31}	d_{31} [10^{-12}m/V]	d_{33}
	Mixed Oxides	97.7	1551	0.670	-0.380	-184	355
	SolGel	96.4	1435	0.554	-0.299	-132	314

G Montanari, AL Costa, S Albonetti, C Galassi.
Nb-doped PZT material by sol-gel combustion. *J. Sol-Gel Sci. Technol.* 2005 **36**,2: 203-211

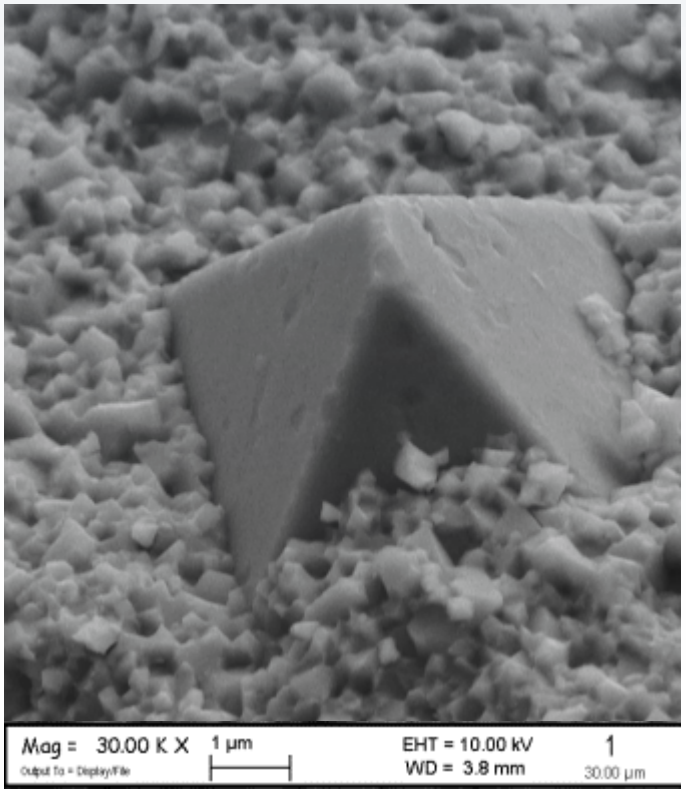
Magnetic phase CFO Cobalt ferrite $CoFe_2O_4$



spinel structure

- **Hard magnetic behaviour**
- **High magnetostriction**

© Lou Perloff / Photo Atlas of Minerals

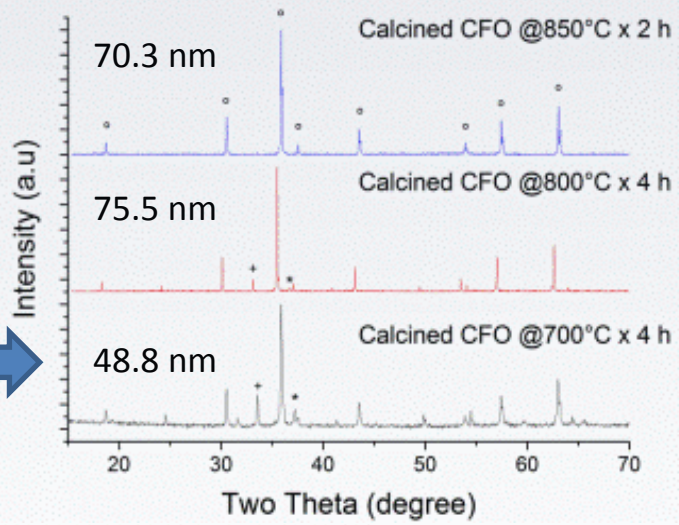



Co_3O_4

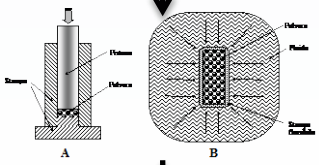

Fe_2O_3

700-1000 °C

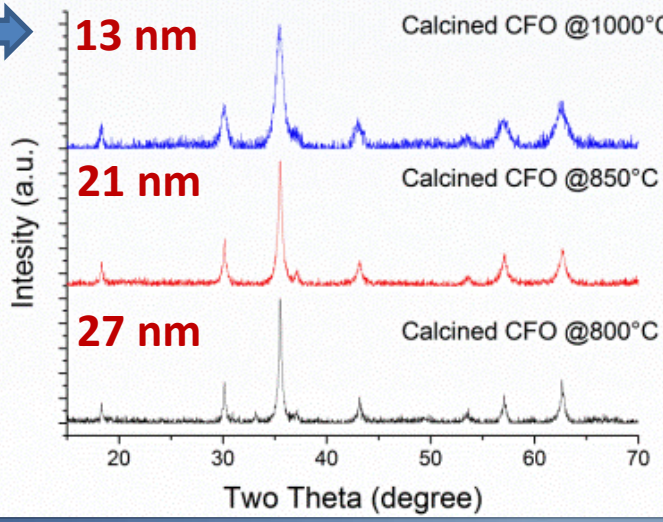
$CoFe_2O_4 + O_2$

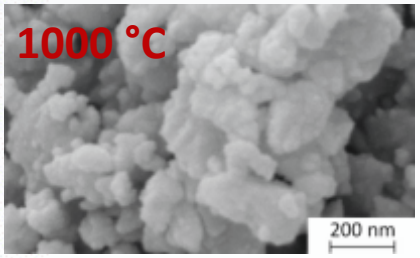


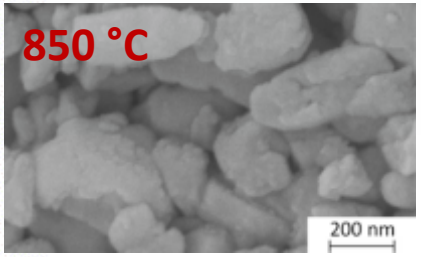
Increase the powders reactivity reducing the average particle size:



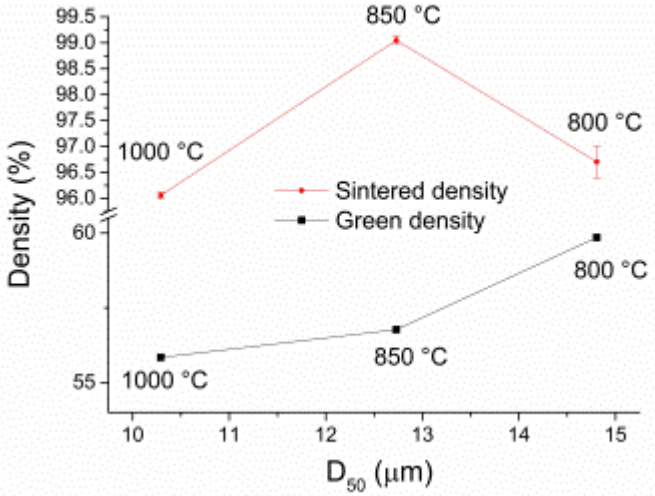
1200°C 2 h

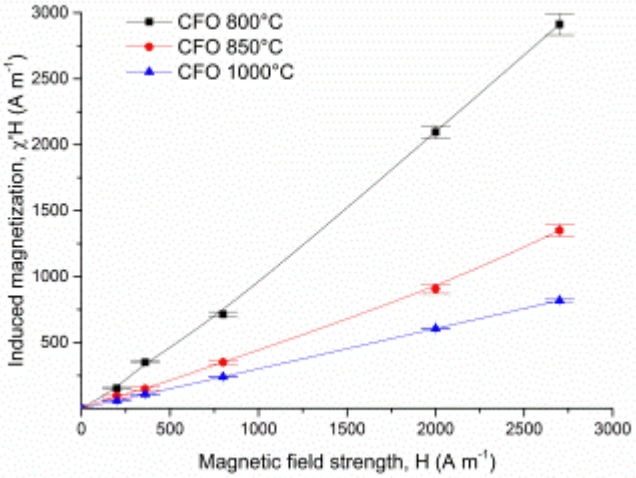


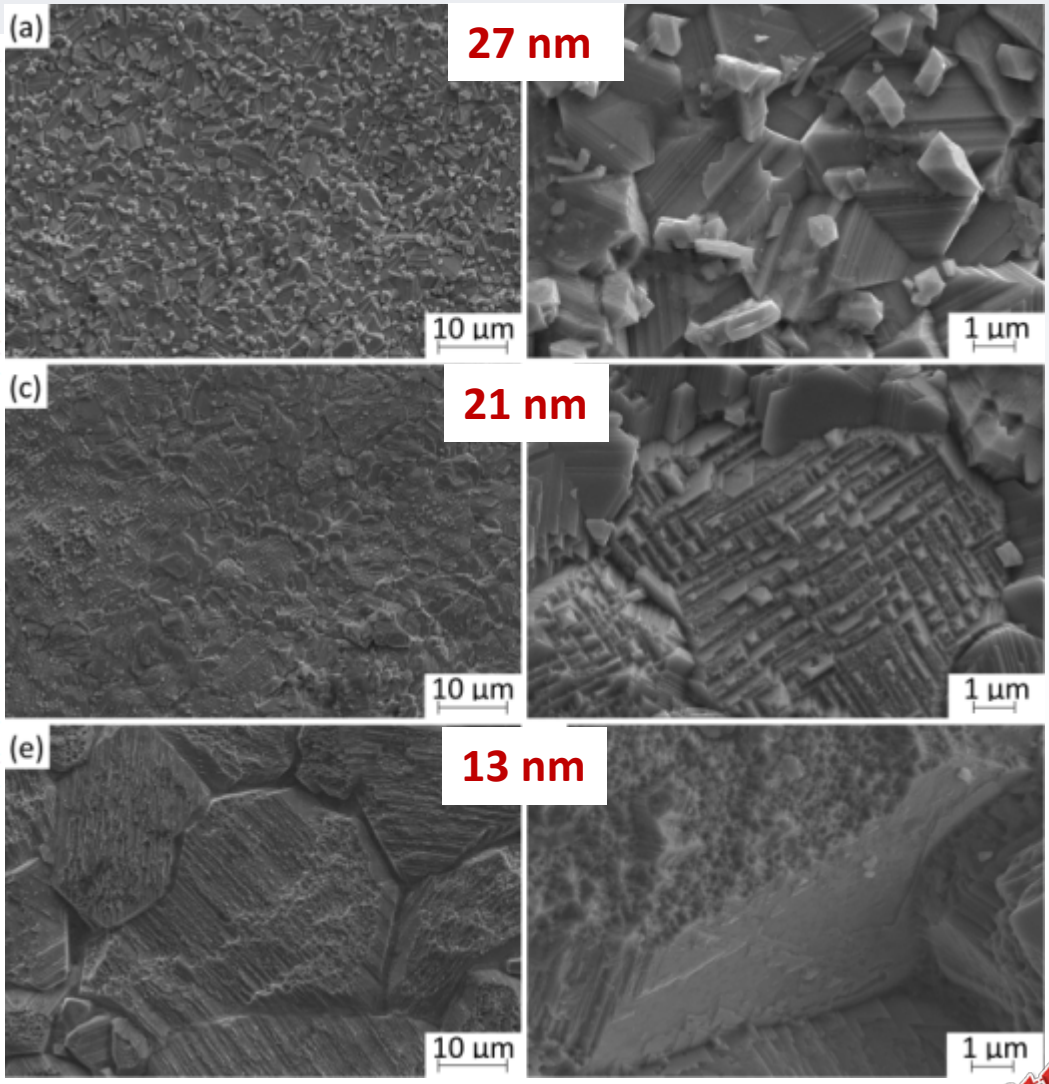




CFO: sintering







Submitted Work

Processing of the composites

Processing related issues

- difference in thermal expansion coefficient
- lead losses

PZTN

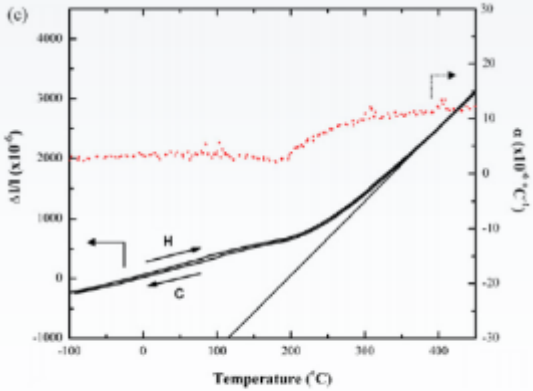


Fig. 2. Thermal expansion ($\Delta l/l$) and thermal expansion coefficient (α) as a function of temperature for $(1-x)$PMN–xPT ceramics: (a) $x = 0.20$, (b) $x = 0.30$ and (c) $x = 0.35$.

CFO

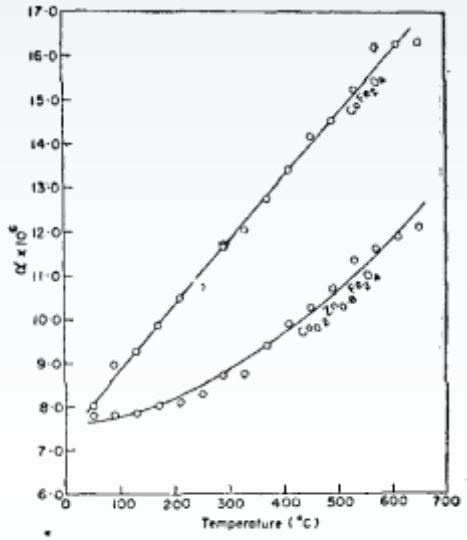
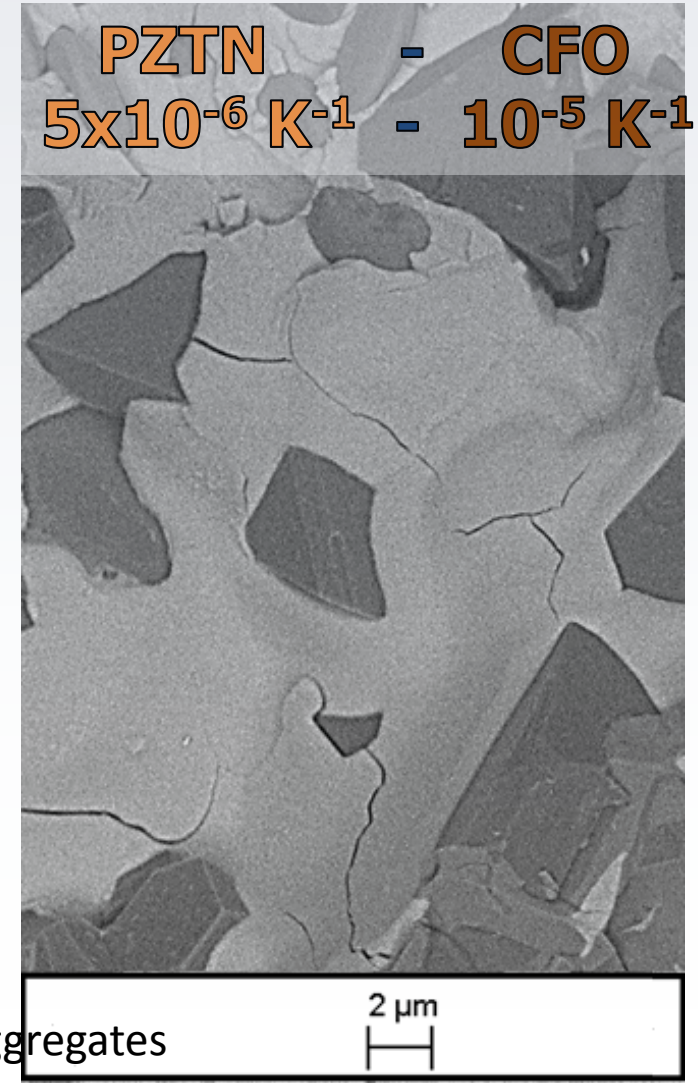
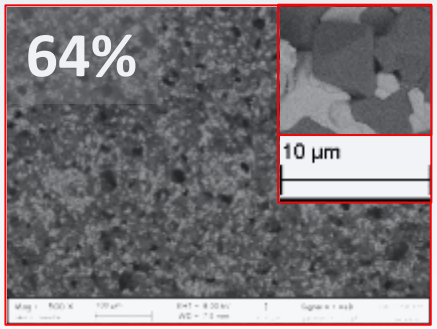
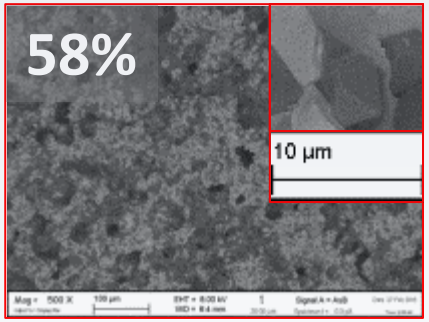
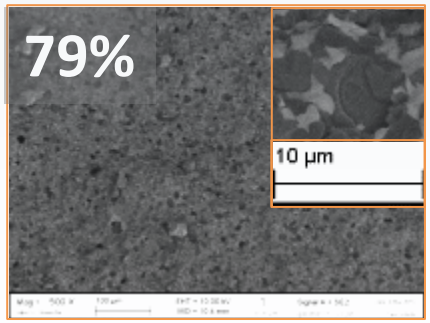
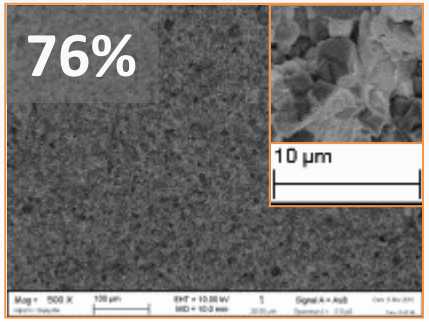
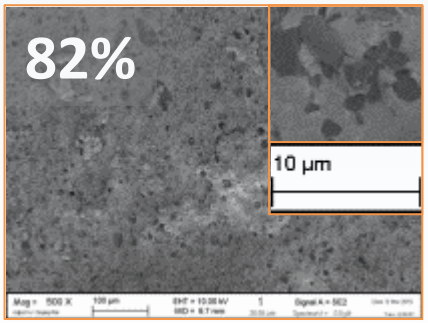
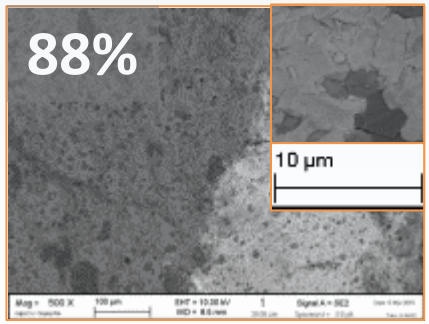
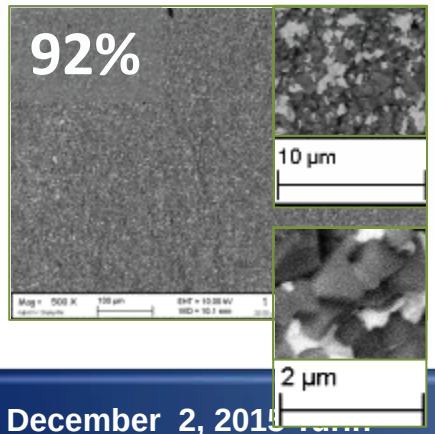
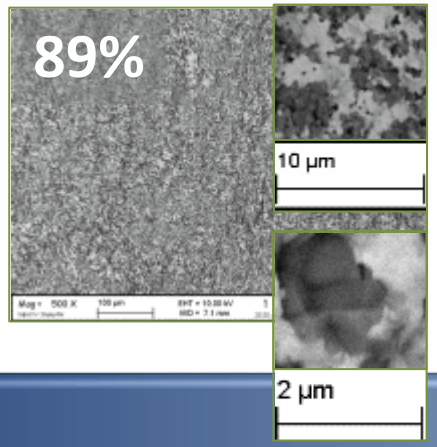
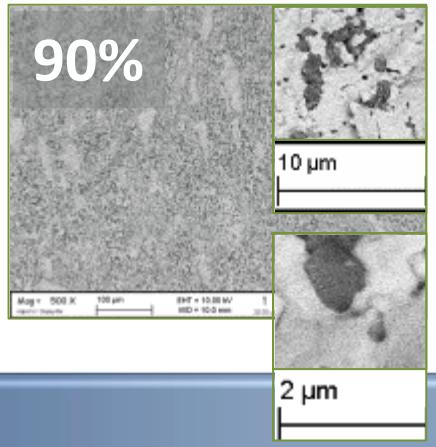
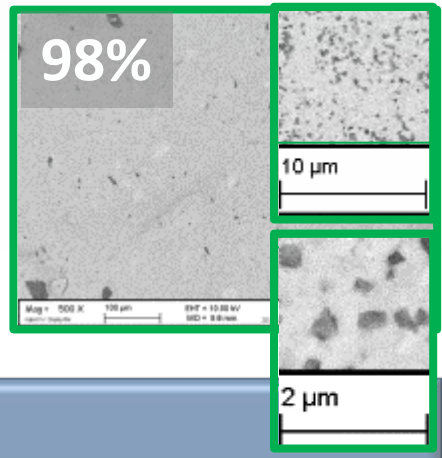


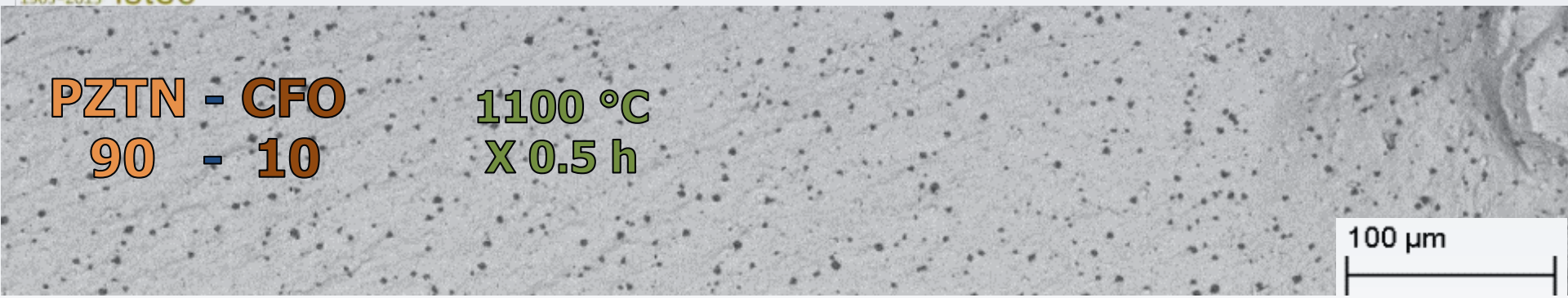
FIG. 1. Variation of the coefficient of thermal expansion of $CoFe_2O_4$ and $Co_{0.9}Zn_{0.8}Fe_2O_4$ with temperature.

Possible solutions

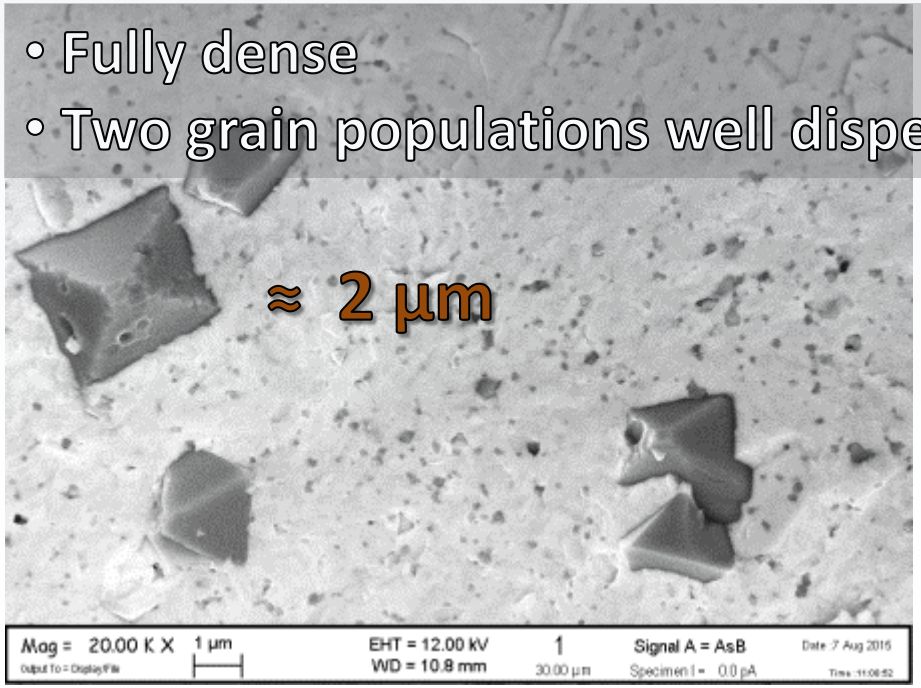
- Reduction of the CFO particle size
- Increasing on the dispersion and distribution of CFO aggregates
- Reduction of the sintering time and temperature

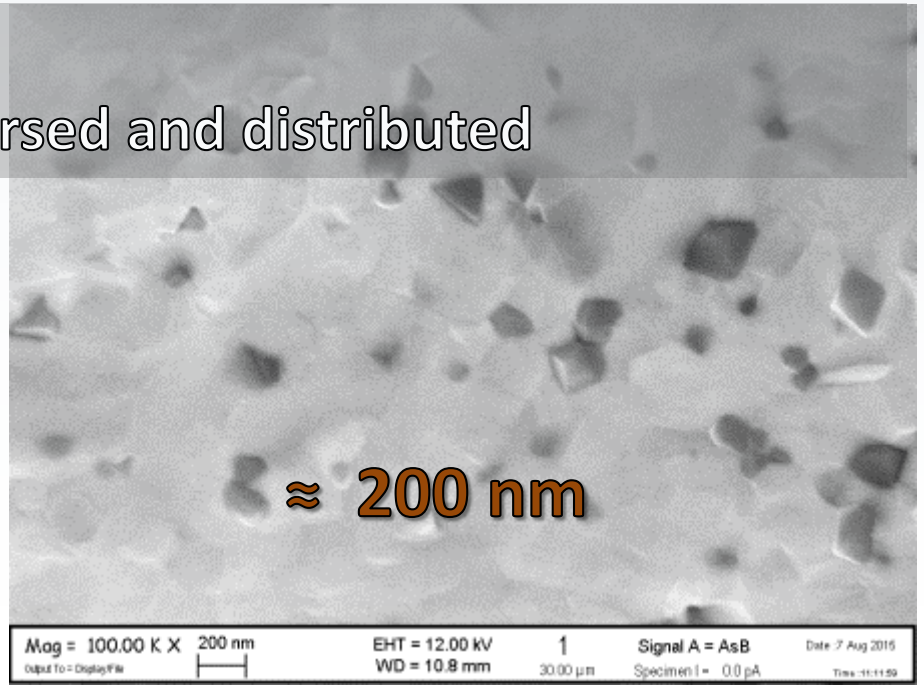


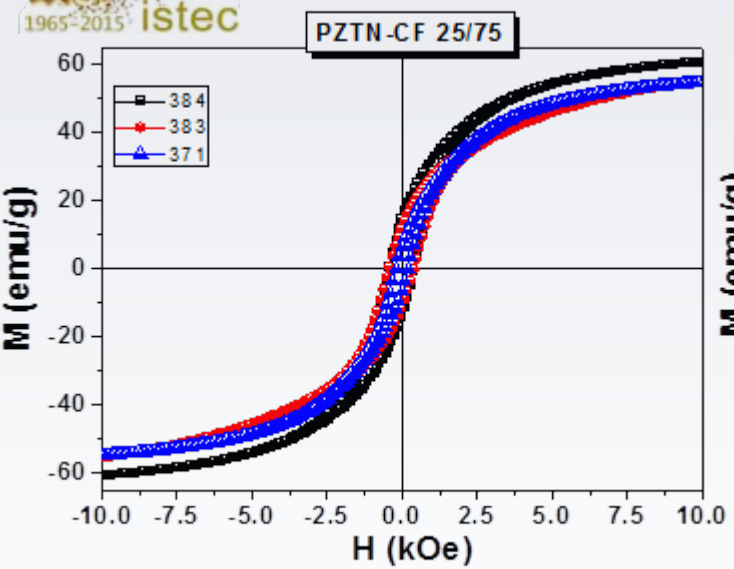
	PZTN - CFO 25 - 75	PZTN - CFO 50 - 50	PZTN - CFO 75 - 25	PZTN - CFO 80 - 20
1250 °C X 2 h			Melting point	Melting point
1200 °C X 2 h				
1100 °C X 0.5 h				

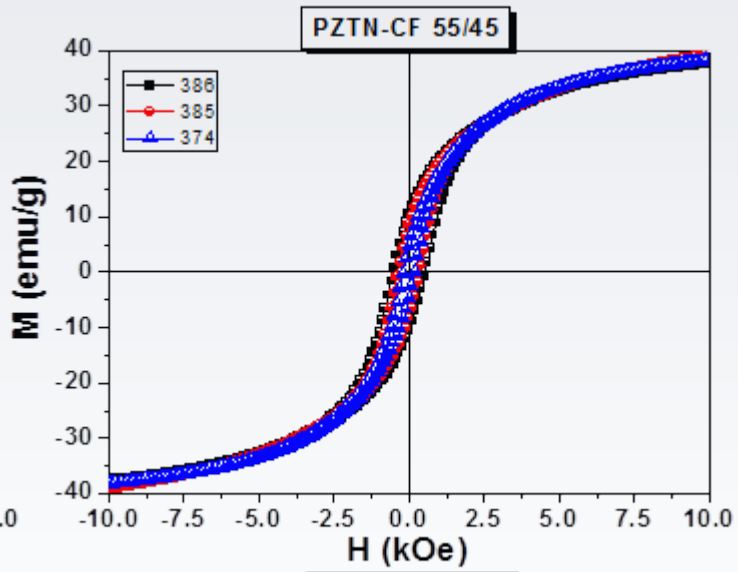


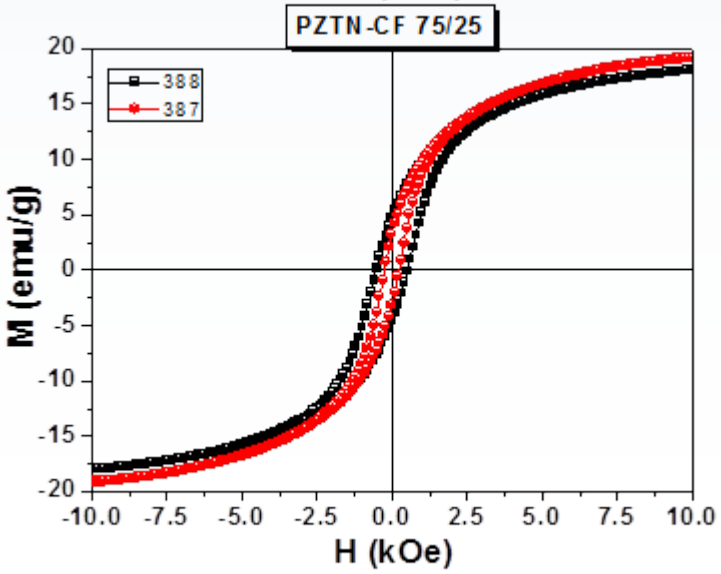
- Fully dense
- Two grain populations well dispersed and distributed

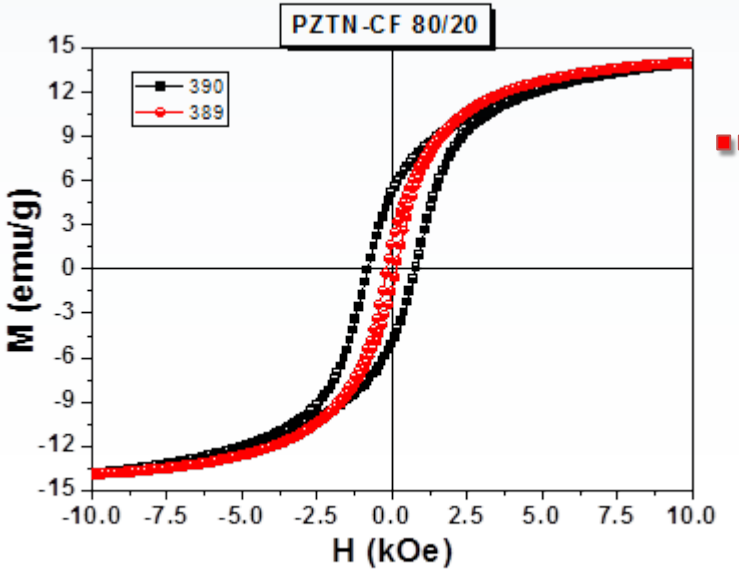












- ✓ Ferromagnetic properties were checked
- Ferroelectric properties will be analysed
- Magnetic-electric coupling will be analysed

Work in Progress

Magneto-dielectric composite materials based on $TiO_2/CoFe_2O_4$ system

These materials were used as substrate for Miniaturized Microstrip Antennas.

Magneto-Dielectric Bulk

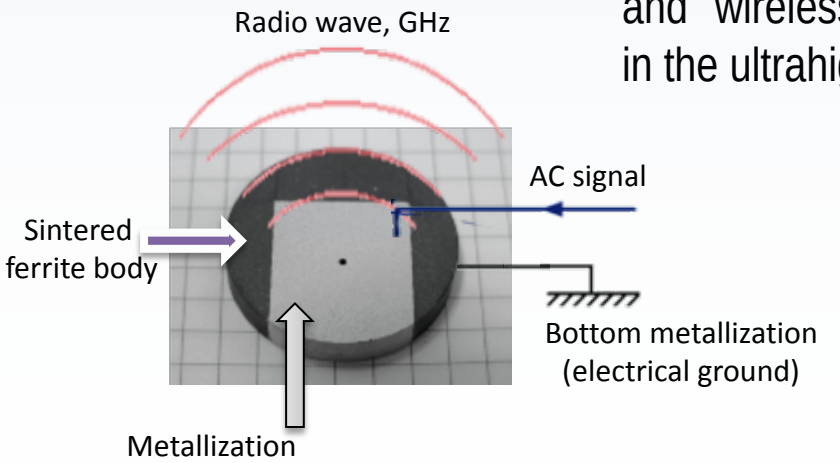
… The aim is to improve the magnetodielectric properties for wearable and wireless applications in the ultrahigh frequency.

- Radiation efficiency
- Bandwidth

miniaturization factor

$$n = \sqrt{\frac{\mu_r}{\varepsilon_r}}$$

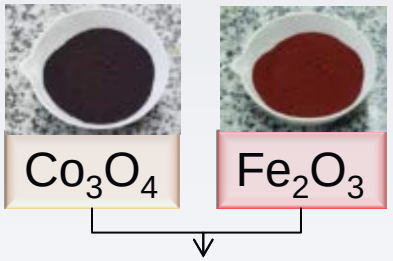
- Stored energy
- Radiated power

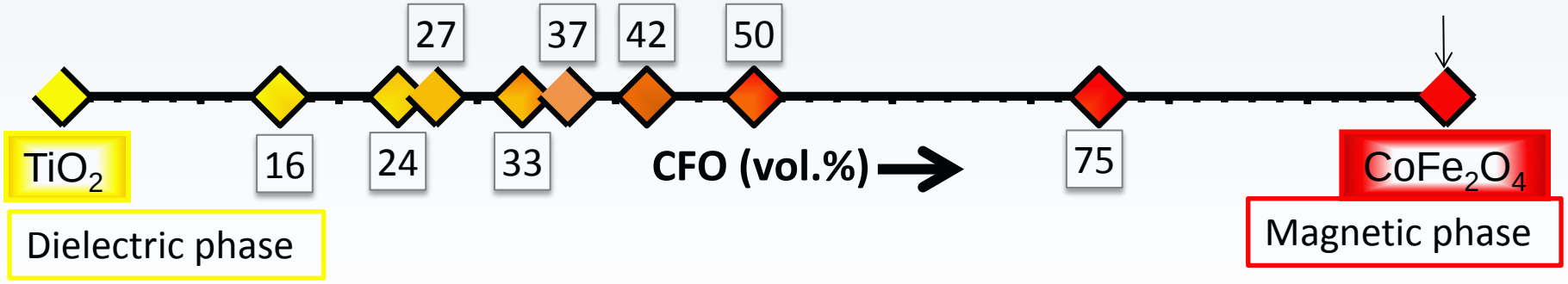


Printed antenna with diameter 31.5 mm

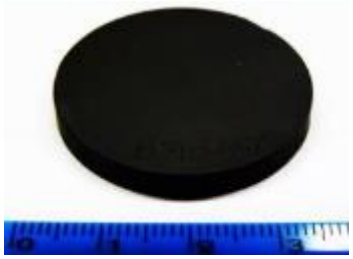
[] **P Galizia**, et al. *"Microstructure development in novel titania-cobalt ferrite ceramic materials"* Ceram. Inter. 2015

The samples were prepared by **solid state reaction** starting from commercial powders:





Sintered in air at 1200 °C for 2 h

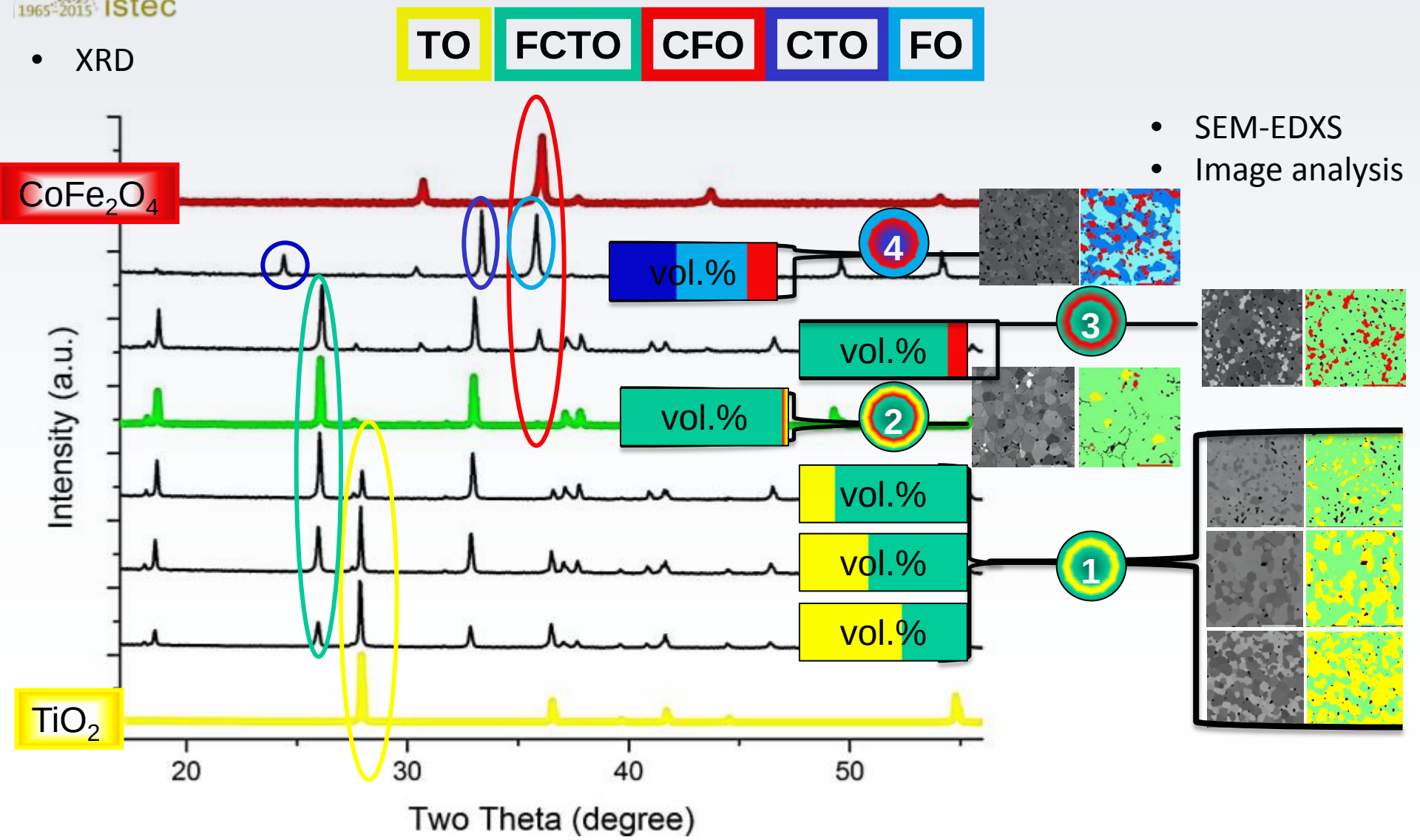


[] **P Galizia**, et al. *"Microstructure development in novel titania-cobalt ferrite ceramic materials"* Ceram. Inter. 2015

- XRD

TO FCTO CFO CTO FO

- SEM-EDXS
- Image analysis



[] **P Galizia**, et al. *"Microstructure development in novel titania-cobalt ferrite ceramic materials"* Ceram. Inter. 2015

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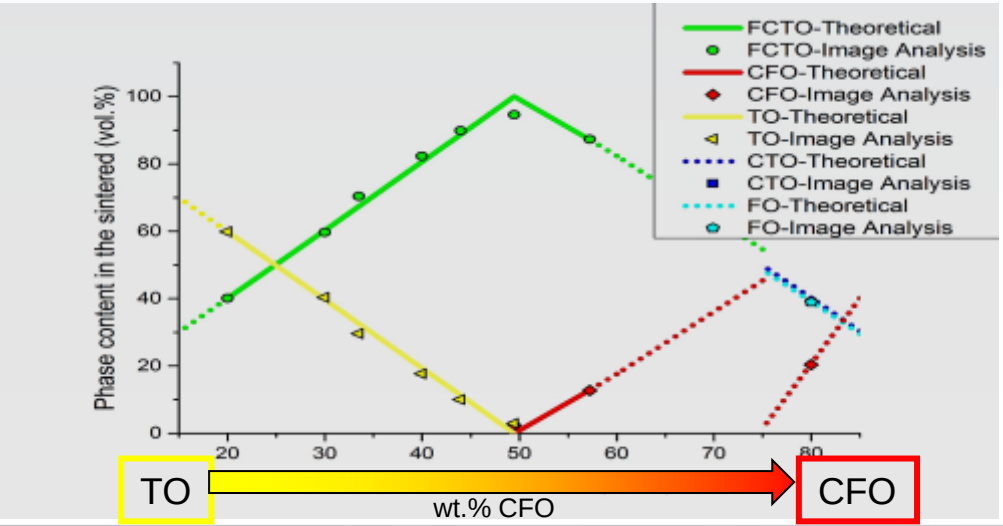
Table 2

TO CFO FCTO CTO FO TO CFO

$$a\mathrm{TiO_2}+b\mathrm{CoFe_2O_4}\rightarrow c\mathrm{Fe_2CoTi_3O_{10}}+d\mathrm{CoTiO_3}+e\mathrm{Fe_2O_3}+f\mathrm{TiO_2}+g\mathrm{CoFe_2O_4}$$

Class	a/b	c	d	e	f	g
I	3–11.75	$=b$	$=0$	$=0$	$=a-3b$	$=0$
II	3	$\sim b$	$=0$	$=0$	~ 0	~ 0
III	2.2 – 3	$=1/3a$	$=0$	$=0$	$=0$	$=b-1/3a$
IV	0.73	$=0$	$=a$	$=a$	$=0$	$=b-a$



Achievement of new electromagnetic properties tailoring magnetic and dielectric phases

▪▪▪ Functional properties will be analysed

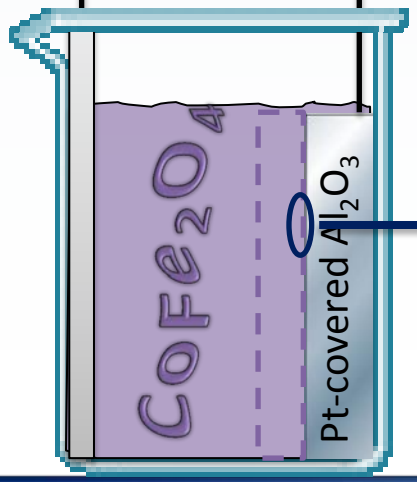
Work in Progress

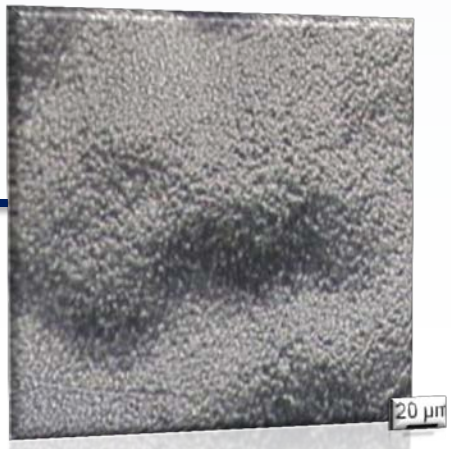
[] **P Galizia**, et al. *"Microstructure development in novel titania-cobalt ferrite ceramic materials"* Ceram. Inter. 2015

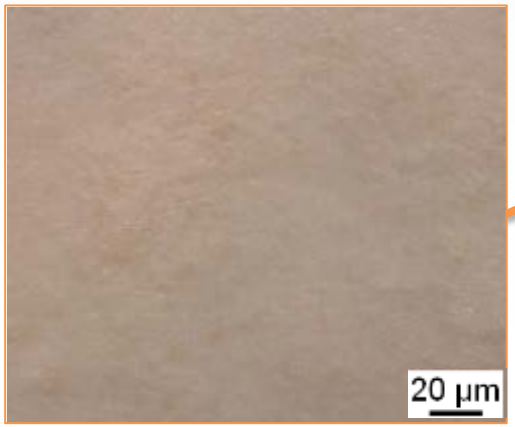
Magnetoelectric composite bilayer films by electrophoretic deposition

- Pt
- $Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$
- $CoFe_2O_4$
- Pt-covered Al_2O_3

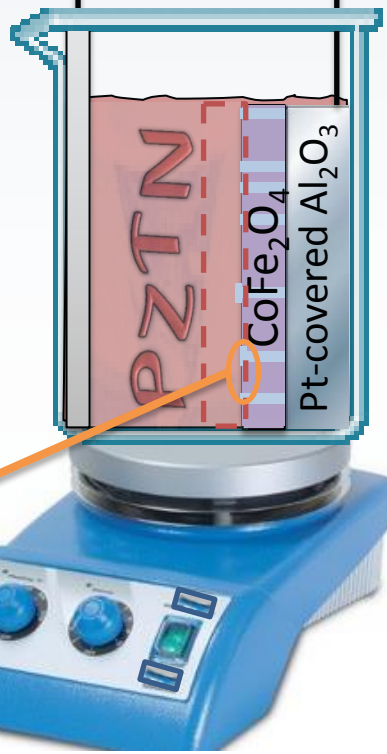
1° EPD



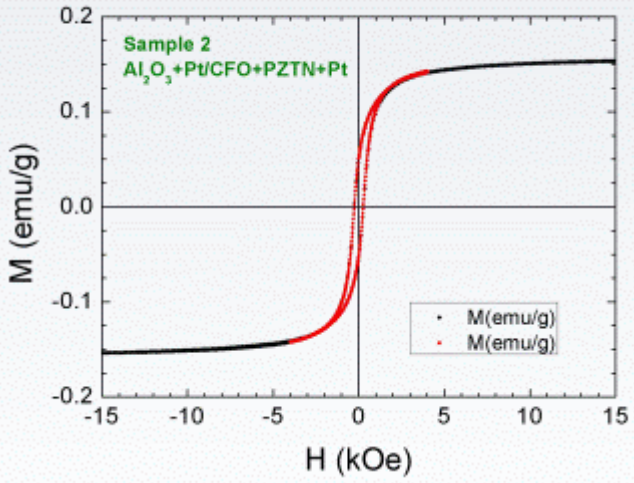


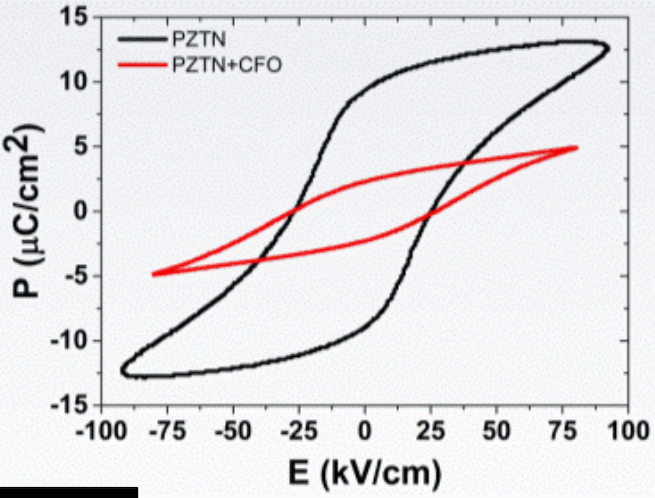


2° EPD

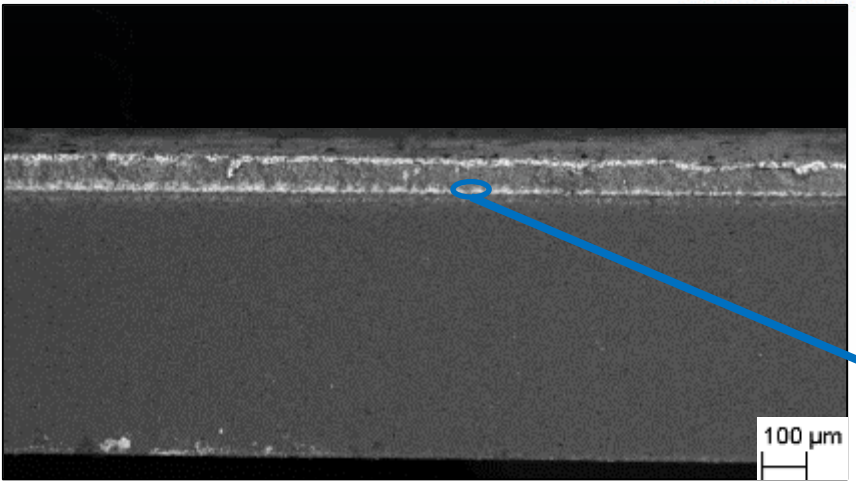


Magnetic and Electric Characterization

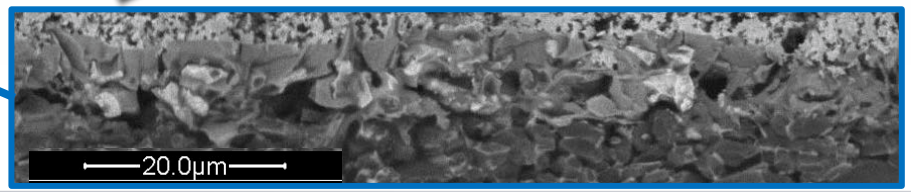




- ✓ Ferromagnetic properties were checked
- ✓ Ferroelectric properties will be analysed
- … Magnetic-electric coupling will be analysed



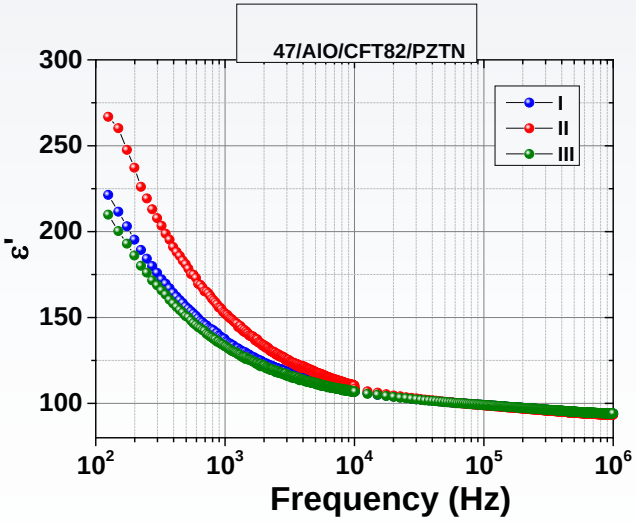
Work in Progress

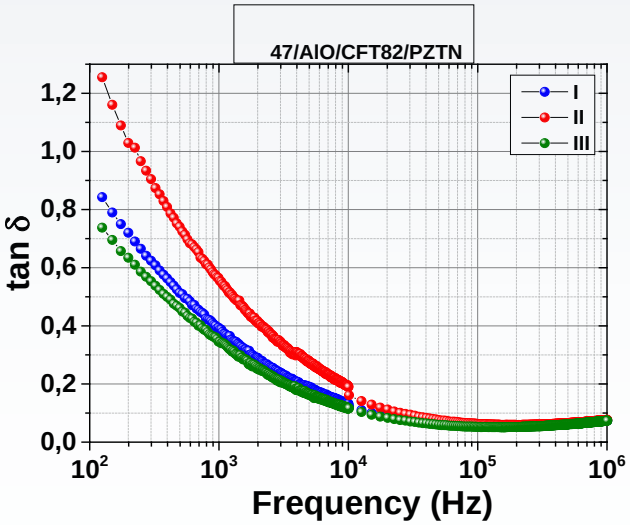


DESIGN AND PREPARATION IN VIEW OF MULTIFUNCTIONALITY

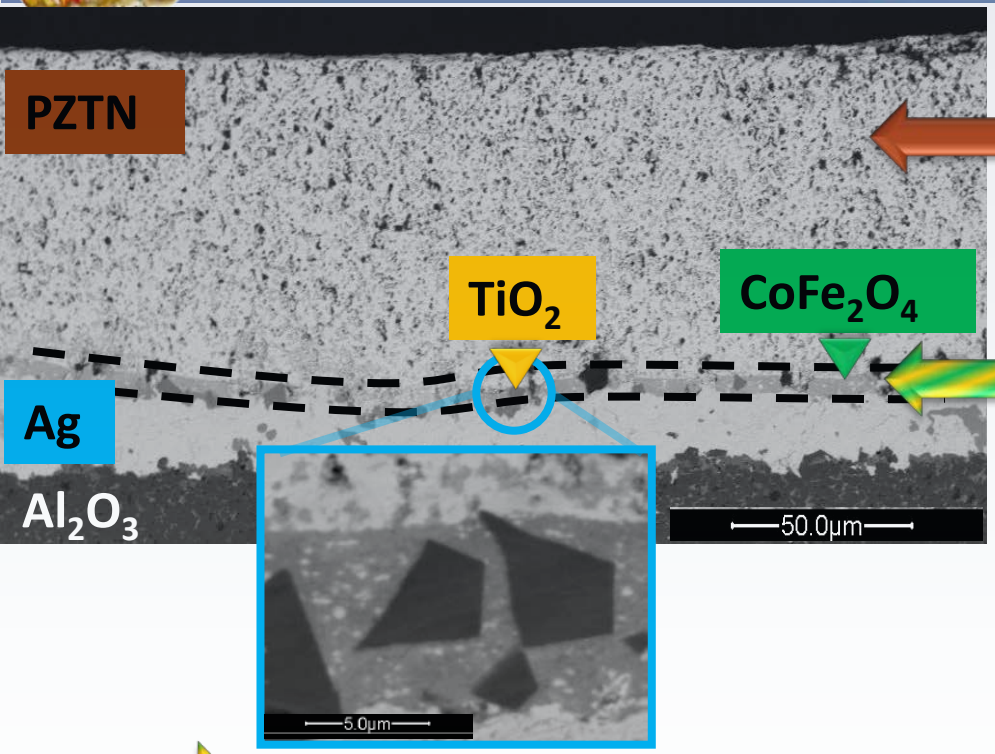
1° layer: Co-deposition of titanium oxide and cobalt ferrite nanoparticles

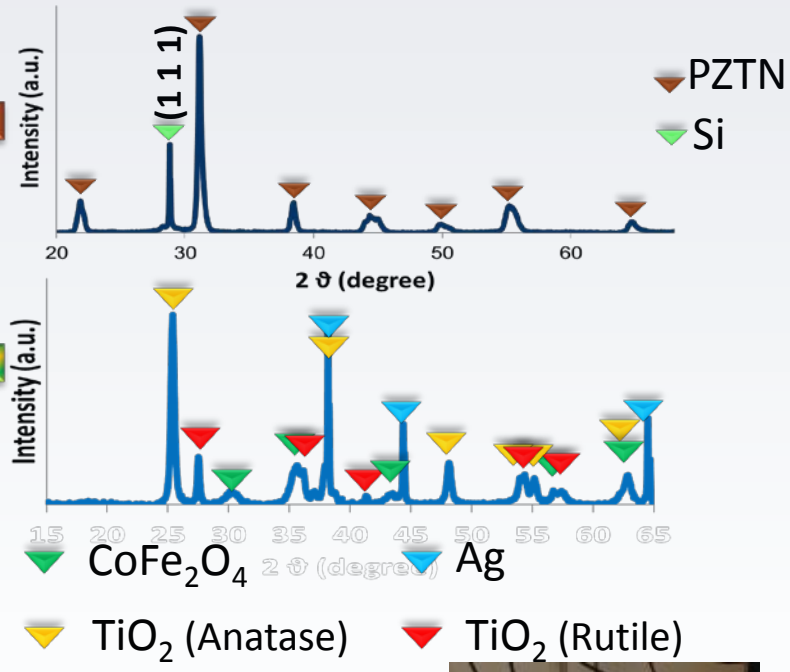
2° layer: deposition of Nb-doped lead titanate zirconate





[] **P Galizia**, et al. *"Bilayer thick structures based on $CoFe_2O_4/TiO_2$ composite and niobium-doped PZT obtained by electrophoretic deposition"* J. Eur. Cer. Soc. 2016; **36**, 2: 373–380.





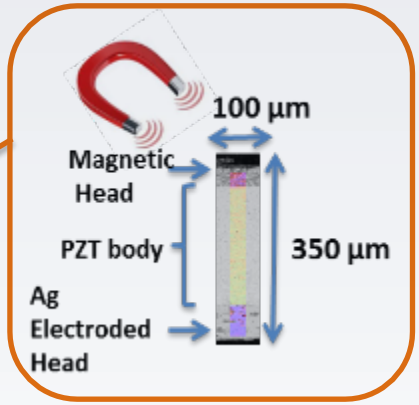
CFO/TO: 98% relative density; 25vol% TiO_2; 75vol% CFO

PZTN: 95% relative density

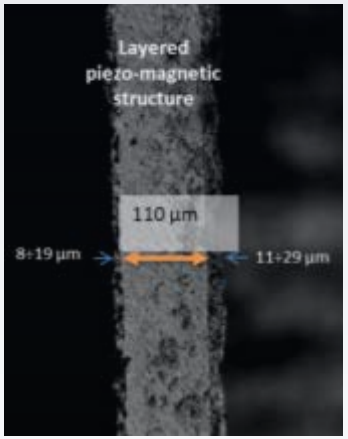
Piezoelectric properties

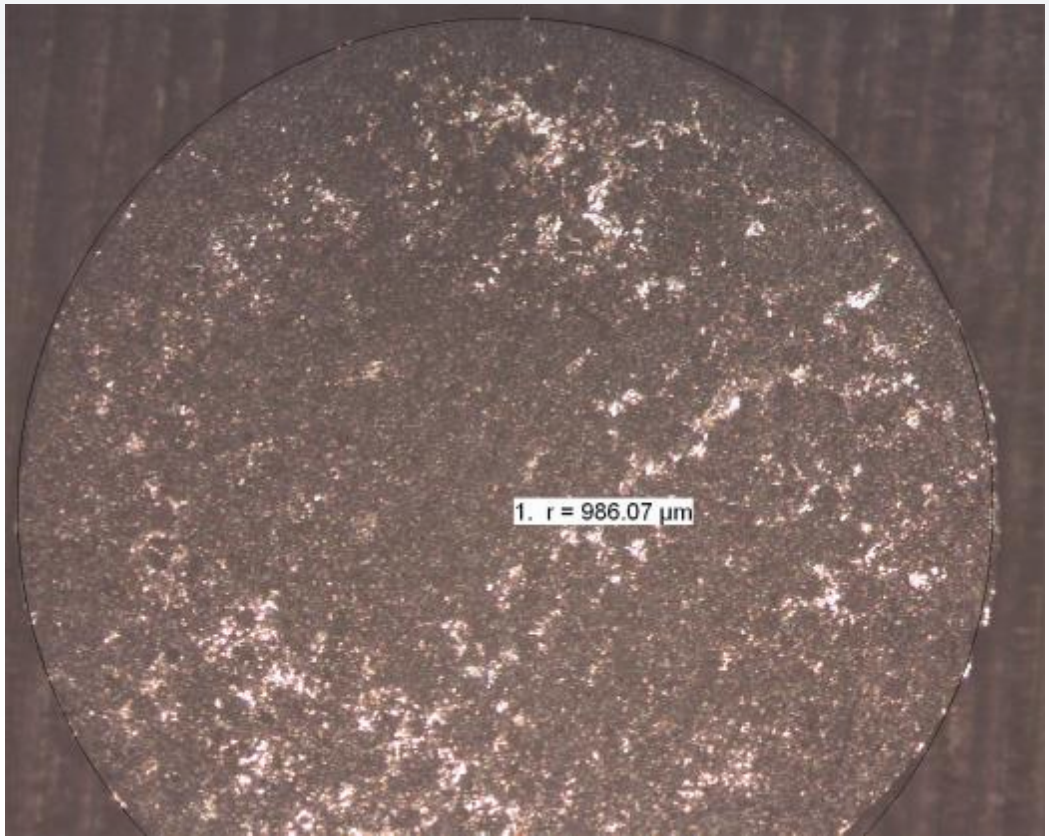
[] **P Galizia**, et al. *"Bilayer thick structures based on $CoFe_2O_4/TiO_2$ composite and niobium-doped PZT obtained by electrophoretic deposition"* J. Eur. Cer. Soc. 2016; **36**, 2: 373–380.

BY TAPE CASTING …



Piezo-magnetic structures





Work in Progress

Miniaturized actuator

CONCLUSIONS

1. The "Influence of milling and calcination temperature on the microstructure of cobalt ferrite" was studied. The results have been submitted.

2. Bulk particulate Nb-doped PZT - cobalt ferrite ceramic composites have been developed, but the functional characterization is still in progress.

3. Novel in-situ particulate composites were produced by combining cobalt ferrite and titanium dioxide. The results on microstructure development have been published, but the functional characterization is still in progress.

4. Electrophoretic deposition was used to produce multifunctional thick films:
   - "Bilayer thick structures based on $CoFe_2O_4/TiO_2$ composite and niobium-doped PZT obtained by electrophoretic deposition" have been produced and the results have been published.
   - PZTN-CFO thick films are under developing

5. Next year, the main research activity will aim to "***study the multiphysics interactions***"

Thank you for your attention