Magnetoelectric composite bilayer films by electrophoretic deposition

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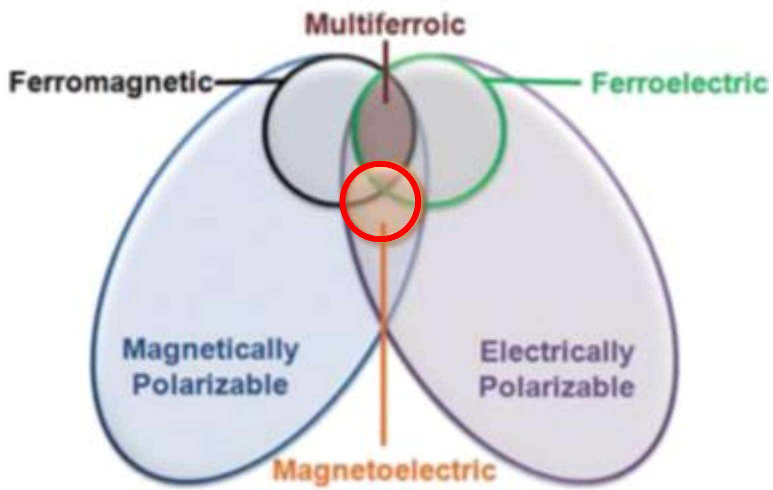
Magnetoelectric composite bilayer films by electrophoretic deposition

MagnetoElectric (ME) effect → change of the polarisation (P) through a magnetic field (H) or the converse ME effect → change of the magnetisation (M) through an electric field (E)



Venn diagram representing the overlap of physical properties in multiferroic materials

G. Schileo Progress in Solid State Chemistry 41, 87-98, 2013
Nan C. V. et Al. Journal of Applied Physics 103, 031101 2008

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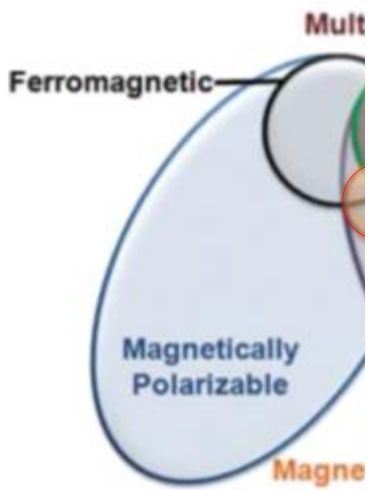

Venn diagram repres
physical properties in

Applications

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

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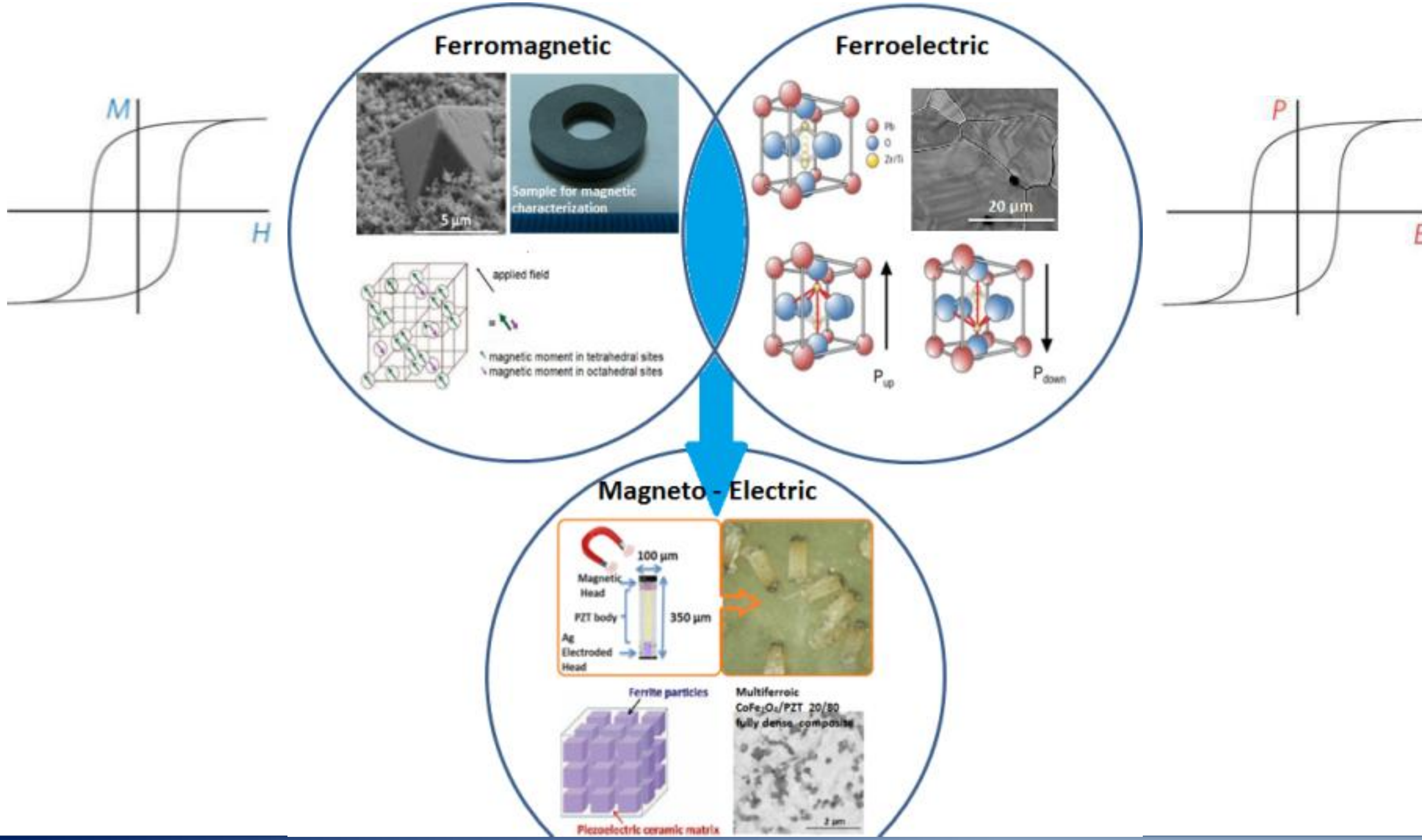

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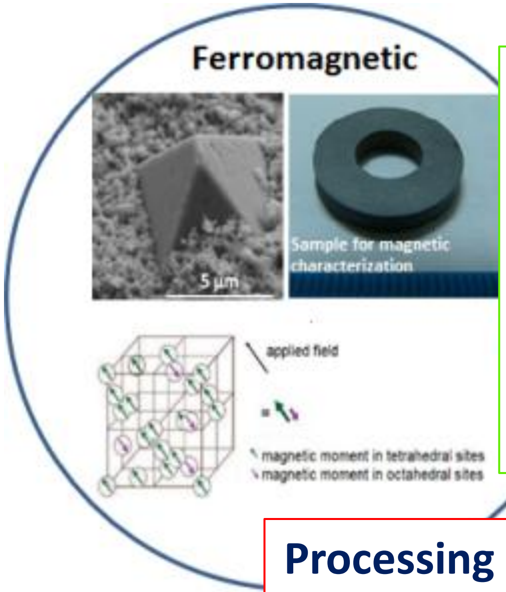

Advantages

- Better electromagnetic performance and new properties, not existing in individual components
- design and preparation in view multifunctionality
- higher degree of freedom in the design

Processing related issues

- low density of the sintered ceramic
- difference in thermal expansion coefficient
- lattice mismatch between the two phases
- atomic interfacial diffusion
- reaction between the two ceramic phases
- magnetic grains can create a conduction path and lead to percolation, making electrical poling impossible.

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The magnetoelectric (ME) coupling is studied by measuring the **induced electric field** (δE) produced by an applied ac magnetic field (δH). The ME voltage coefficient (α_E) is given by:

$$\alpha_E = \delta E/\delta H$$

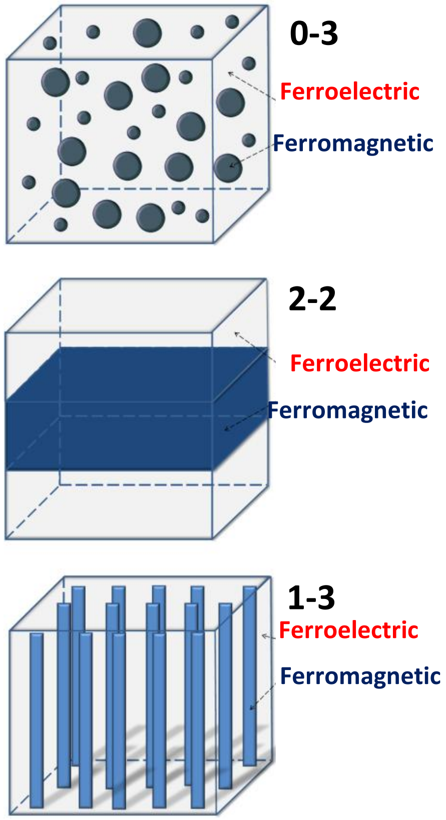
Layout

Single phases

- Ferroelectric
- Ferromagnetic

Composites

- Particulate ceramic composites
- Layred ceramic composites



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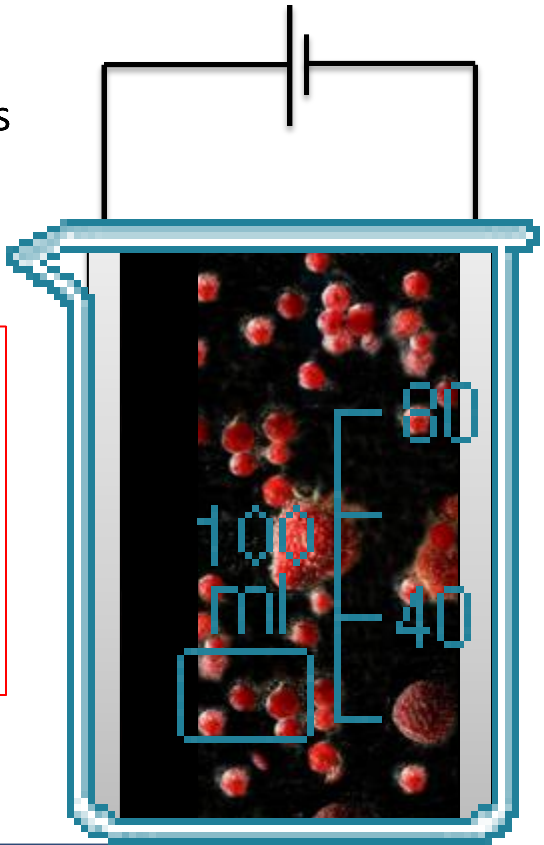
- Applied electric field
- Two conductive electrodes



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

Intrinsic disadvantages
- Generally the liquid medium is an organic solvent. Water causes the evolution of bubbles at the electrodes

- Charged powder particles, dispersed or suspended in a liquid medium

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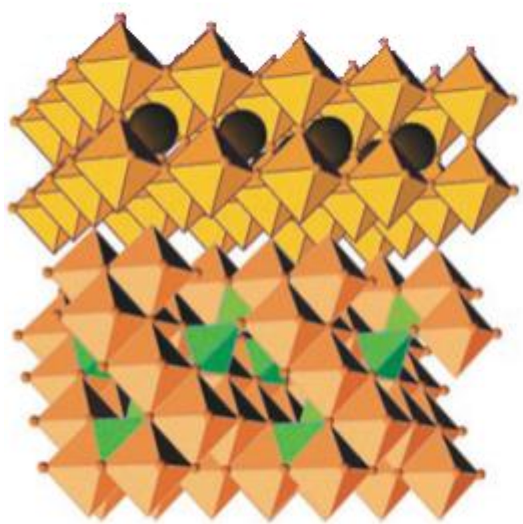
Experimental Work

Heterostructure consisting of bilayer on substrate

- 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

Superlattice of a perovskite (top) and spinel (bottom)

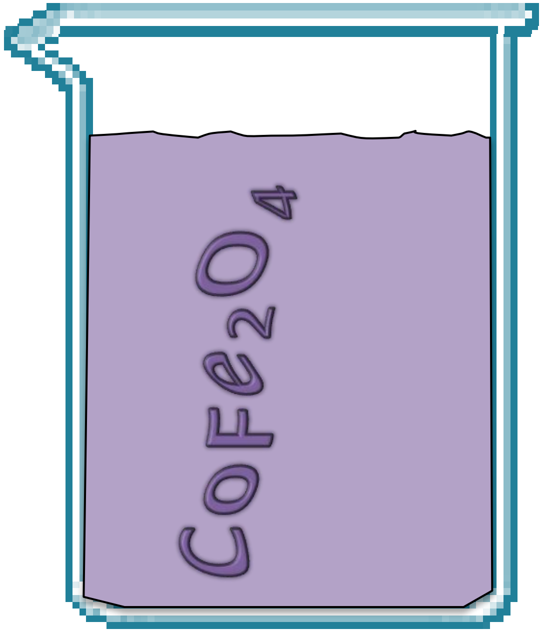


Ferroelectrics crystallize in the **perovskite structure** and it maintain a fraction of the polarisation when the field is removed, after poling

Ferrites crystallize in the **cubic spinel structure**, where metal cations occupy tetrahedral and octahedral interstitial sites of a FCC oxygen sublattice

Before- 1° EPD Processing

- The nanosized $CoFe_2O_4$ suspension was provided by Ce.Ri.Col. (Colorobbia Research Center, Empoli, Italy) with a solid load of 2.5 wt% in diethylene glycol
- The commercial suspension was diluted with absolute ethanol (Fluka) down to the concentration of 0.3 wt% in order to ensure film coagulation during the EPD process



C. Baldisserri, D. Gardini, C. Galassi Key Engineering Materials Vol. 507 (2012) pp 85-88

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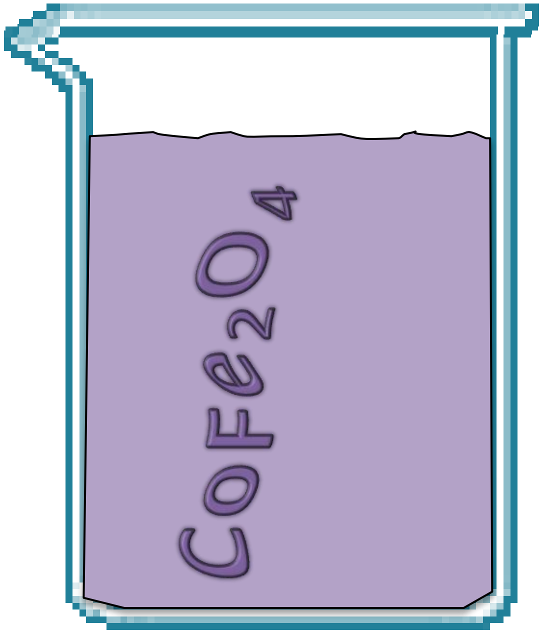
Before- 1° EPD Processing

- The nanosized $CoFe_2O_4$ suspension was provided by Ce.Ri.Col. (Colorobbia Research Center, Empoli, Italy) with a solid load of **2.5 wt%** in diethylene glycol
- The commercial suspension was diluted with absolute ethanol (Fluka) down to the concentration of **0.34 wt%** in order to ensure film coagulation during the EPD process

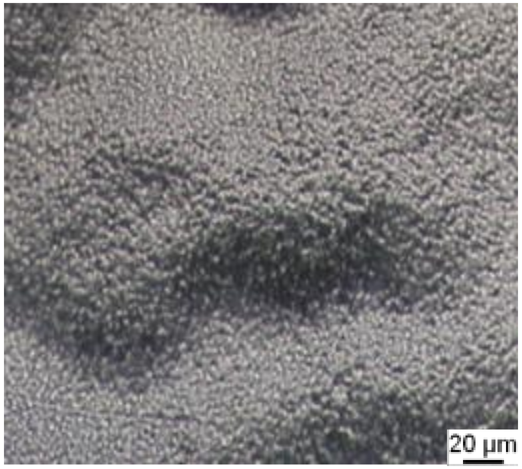
Stoichiometry (spinel) :	**$CoFe_2O_4$**
Particles Density:	**5.27 g cm^{-3}**
Suspension Density:	**0.83 g cm^{-3}**
Solid Loading, wt%:	**0.34**
Particle Size (DLS):	**10.1 nm**
Viscosity:	**56.7 mPa s**
ζ-potential :	**47.5 mV**
Electrical Conductivity:	**15 µS cm^{-1}**



1° EPD Processing

CFO EPD setting:

- plane-parallel cell geometry (1 cm electrodes spacing)
- 20 cm^2 SS secondary electrode
- 2 cm^2 Pt-coated alumina working electrode
- 50 cm^3 of suspension
- cathodic modality
- constant DC potential at 50 V for 100 s



Solid Loading, wt%:	0.34
Particle Size (DLS):	10.1 nm
Viscosity:	56.7 mPa s
ζ-potential :	47.5 mV
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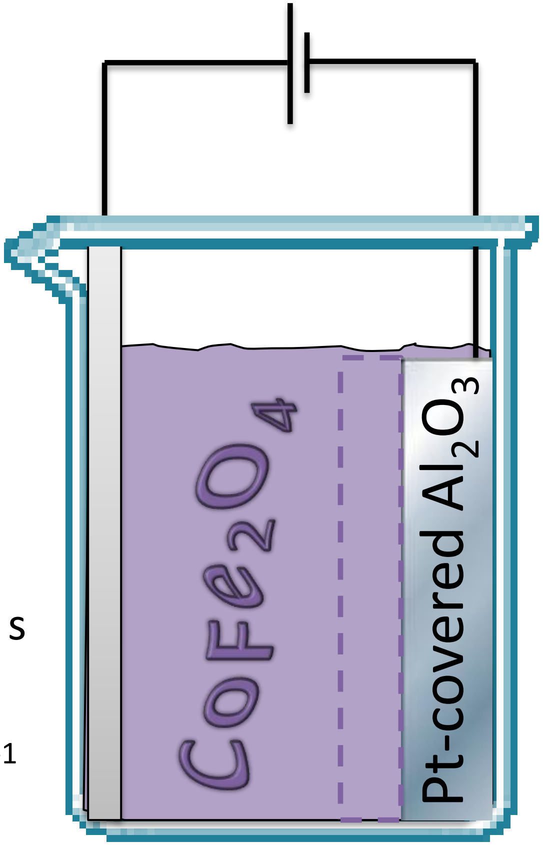

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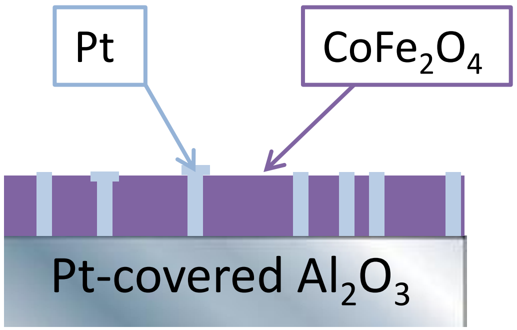
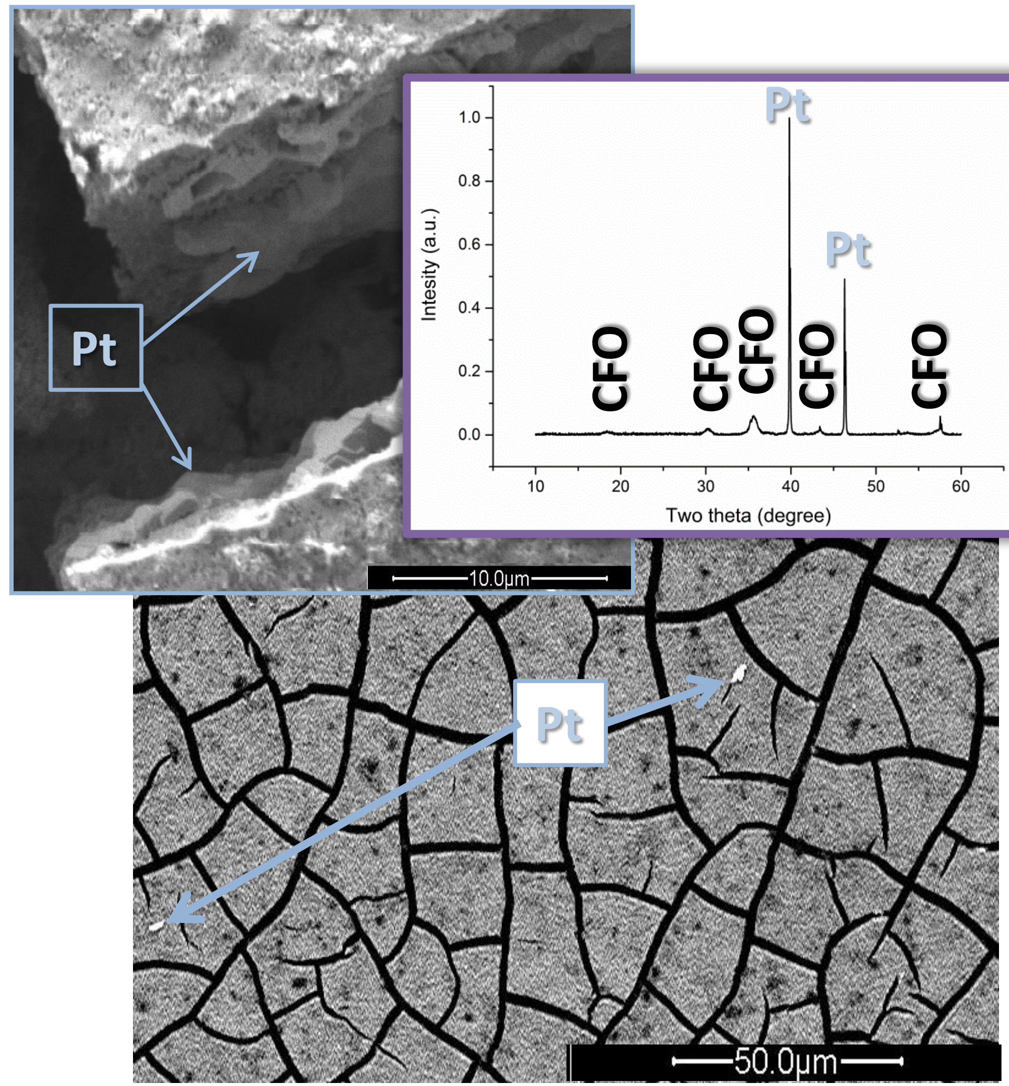
Post- 1° EPD Processing

After EPD:

- Drying in air for 2 days
- Heat treatment at 500 °C for 15 min





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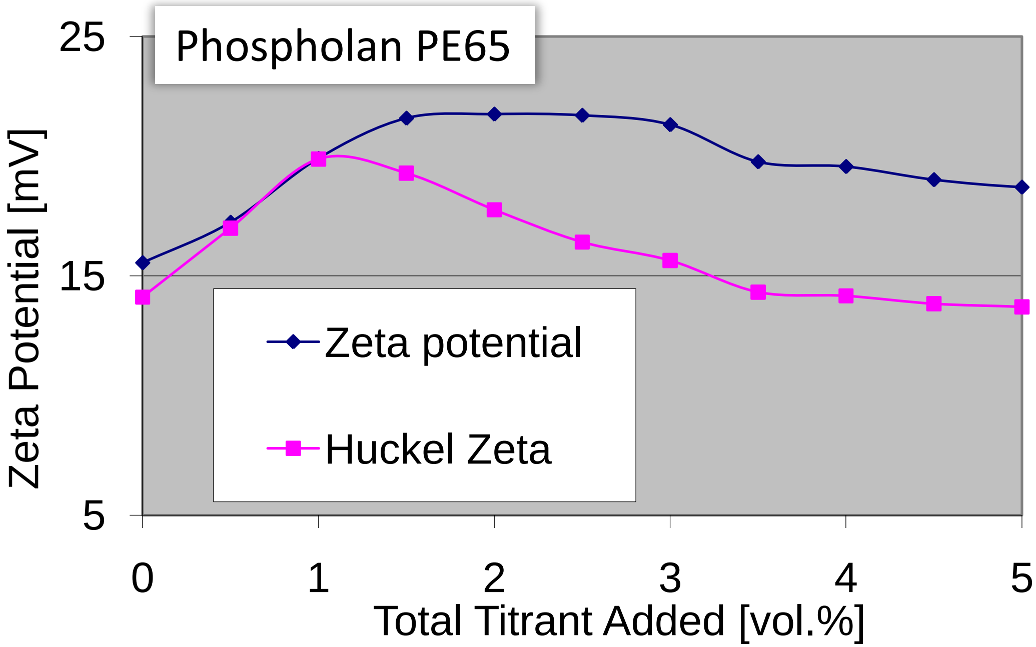
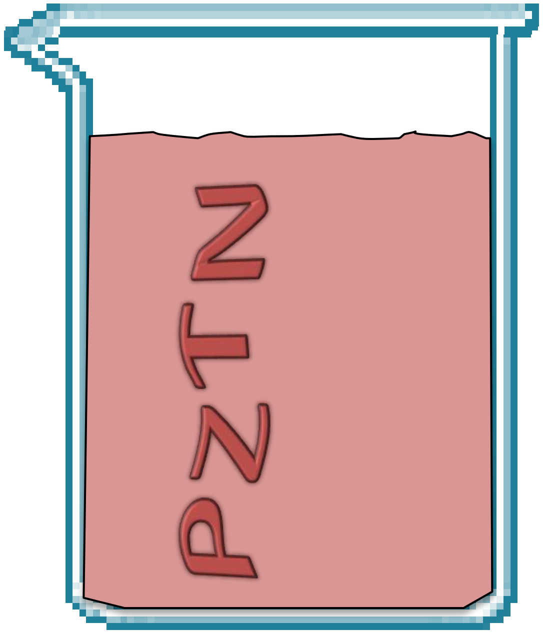
Before- 2° EPD Processing

- Perovskitic powder $Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$ was prepared by the mixed oxides route. The powders were dispersed in absolute ethanol (Fluka) at **1.7 vol%**.

Particles Density:	**8.006 g cm^{-3}**
Suspension Density:	**0.91 g cm^{-3}**
Solid Loading:	**15 wt.%**
Particle Size (DLS):	**185 nm**
Viscosity:	**1.08 mPa s**
ζ-potential :	**15.6 mV**
Electrical Conductivity:	**2 µS cm^{-1}**





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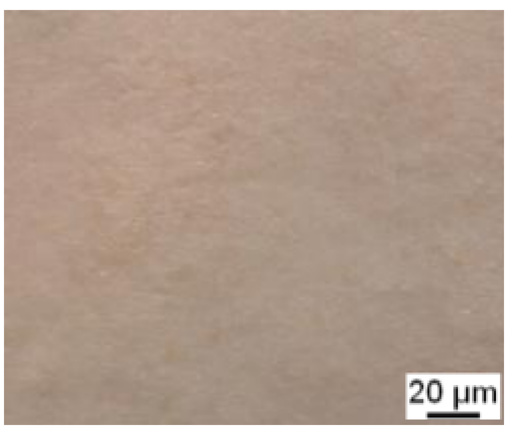
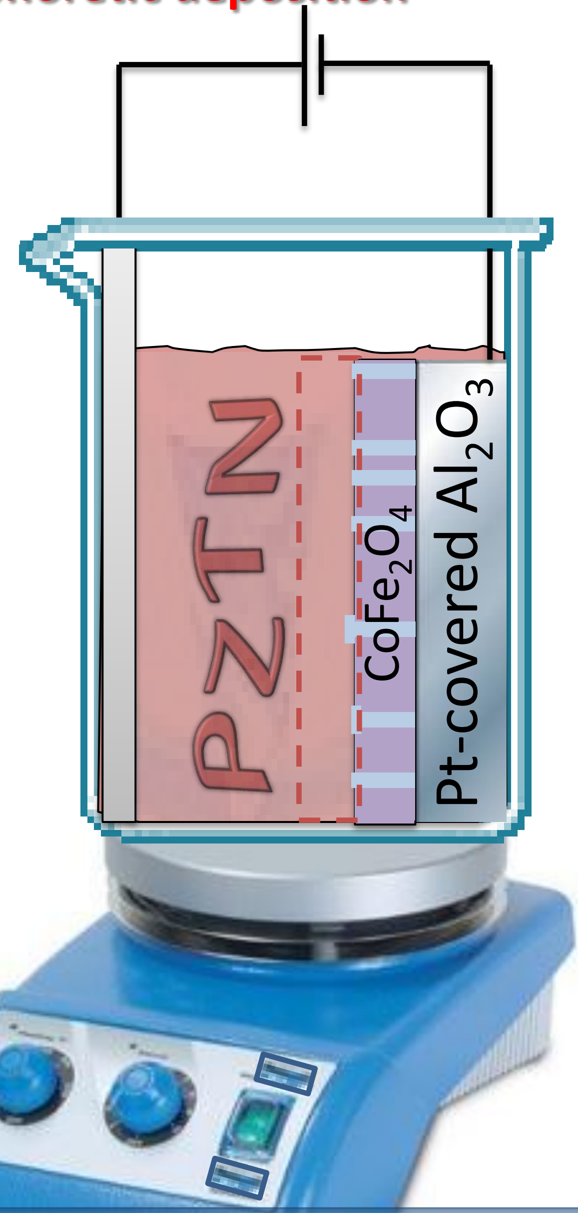
2° EPD Processing

PZTN EPD setting:

- plane-parallel cell geometry (1 cm electrodes spacing)
- 20 cm^2 SS secondary electrode
- 1.5 cm^2 Pt-coated alumina working electrode
- 200 cm^3 of suspension
- cathodic modality
- constant DC potential at 60 V for 15 s
- Magnetic stirring



Solid Loading:	15 wt.%
Particle Size (DLS):	185 nm
Viscosity:	1.08 mPa s
ζ-potential :	15.6 mV
Electrical Conductivity:	2 µS cm^{-1}



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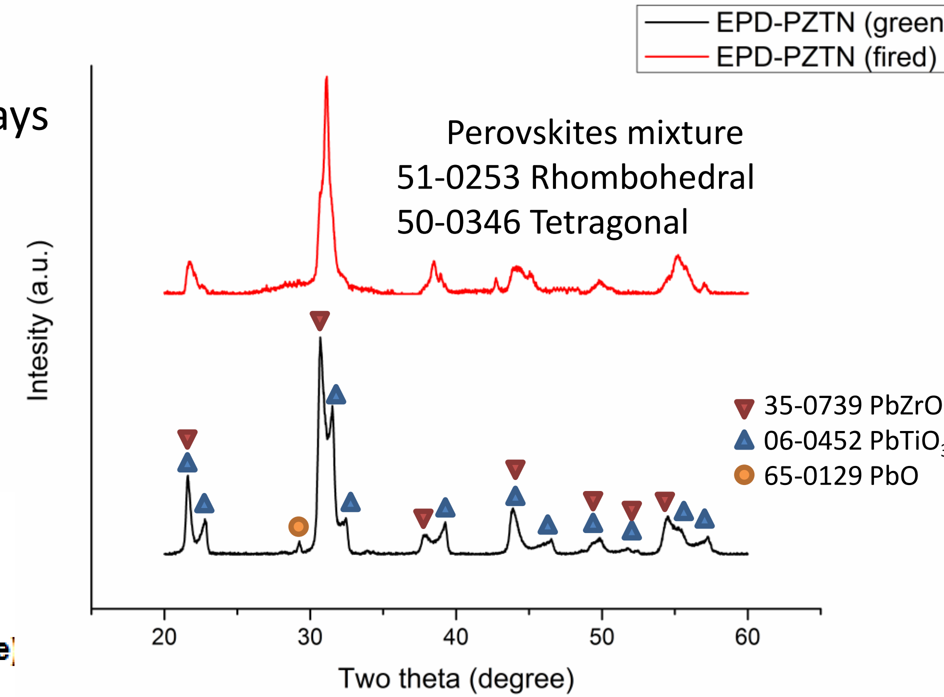
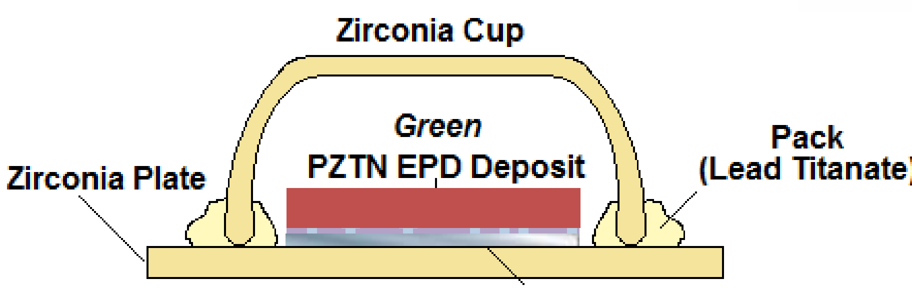
Post- 2° EPD Processing

- Drying in air at room temperature for 2 days
- Heat treatment at 850 °C for 1 h
- Metallization by screen printing
- Heat treatment at 900 °C for 30 min





- Pt
- PZTN
- $CoFe_2O_4$/Pt
- Pt-covered Al_2O_3

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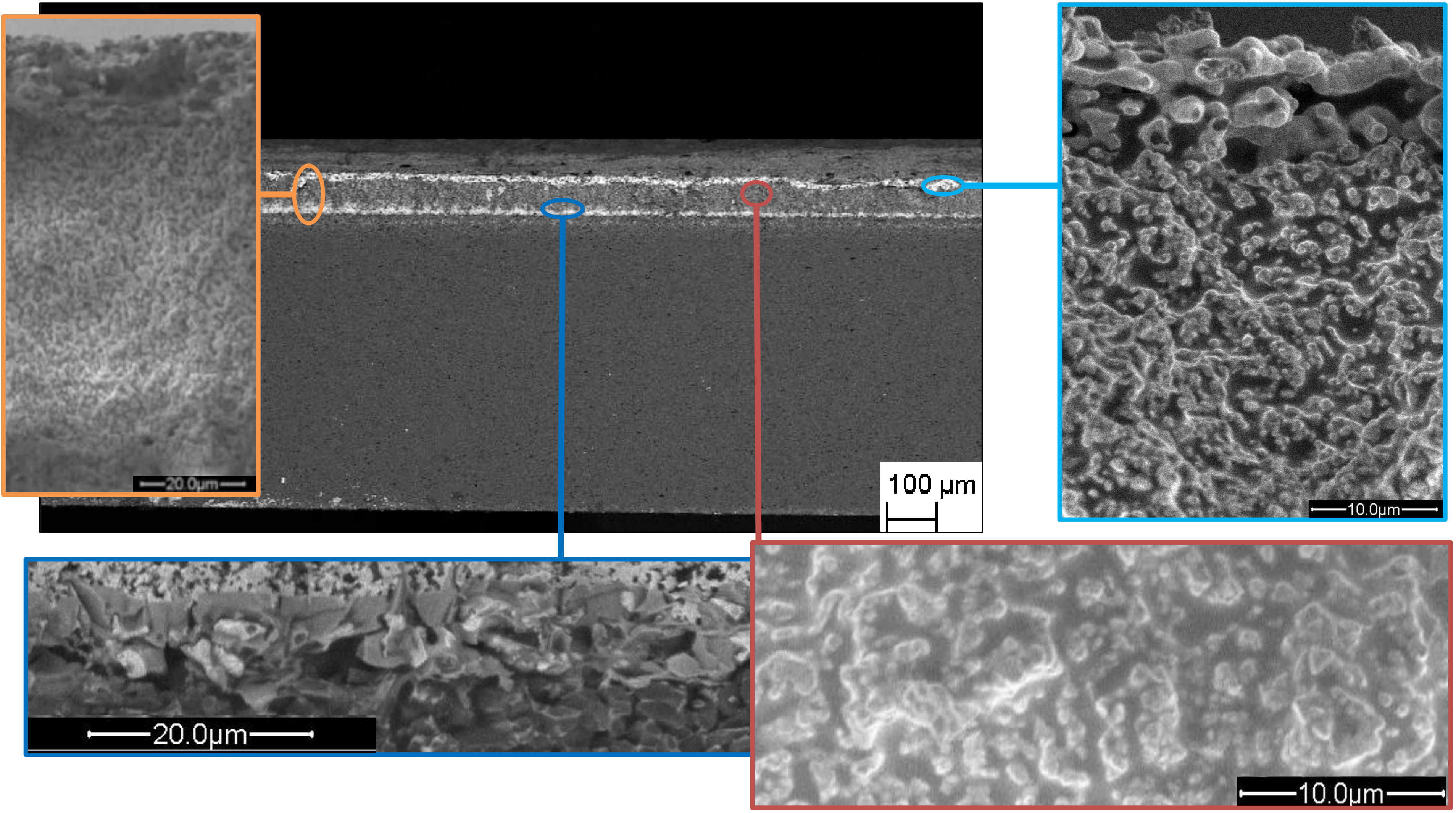
Microstructure



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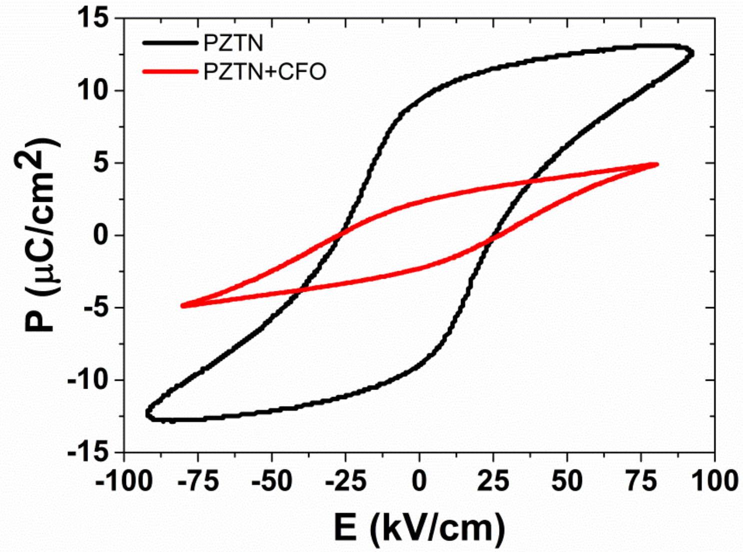
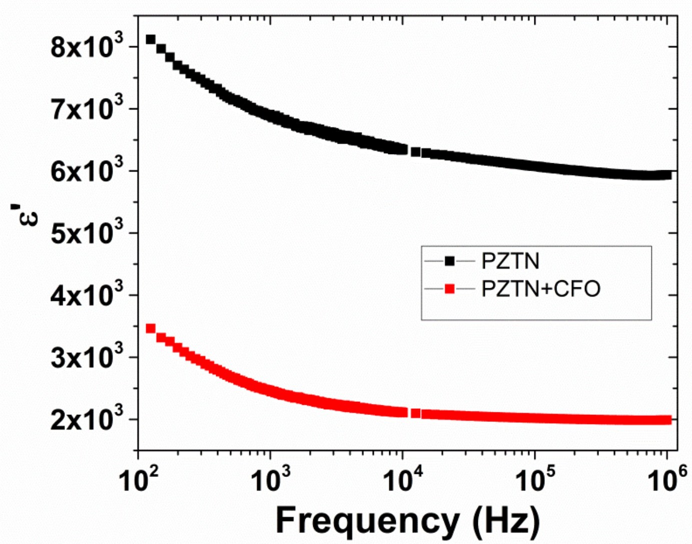
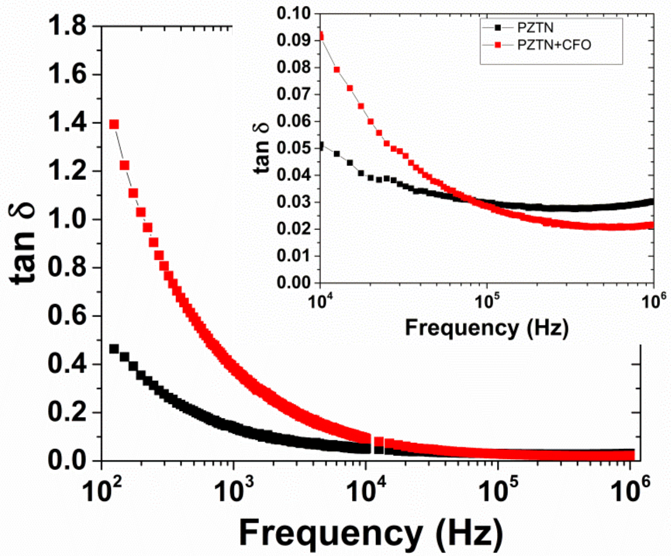
Electric Characterization

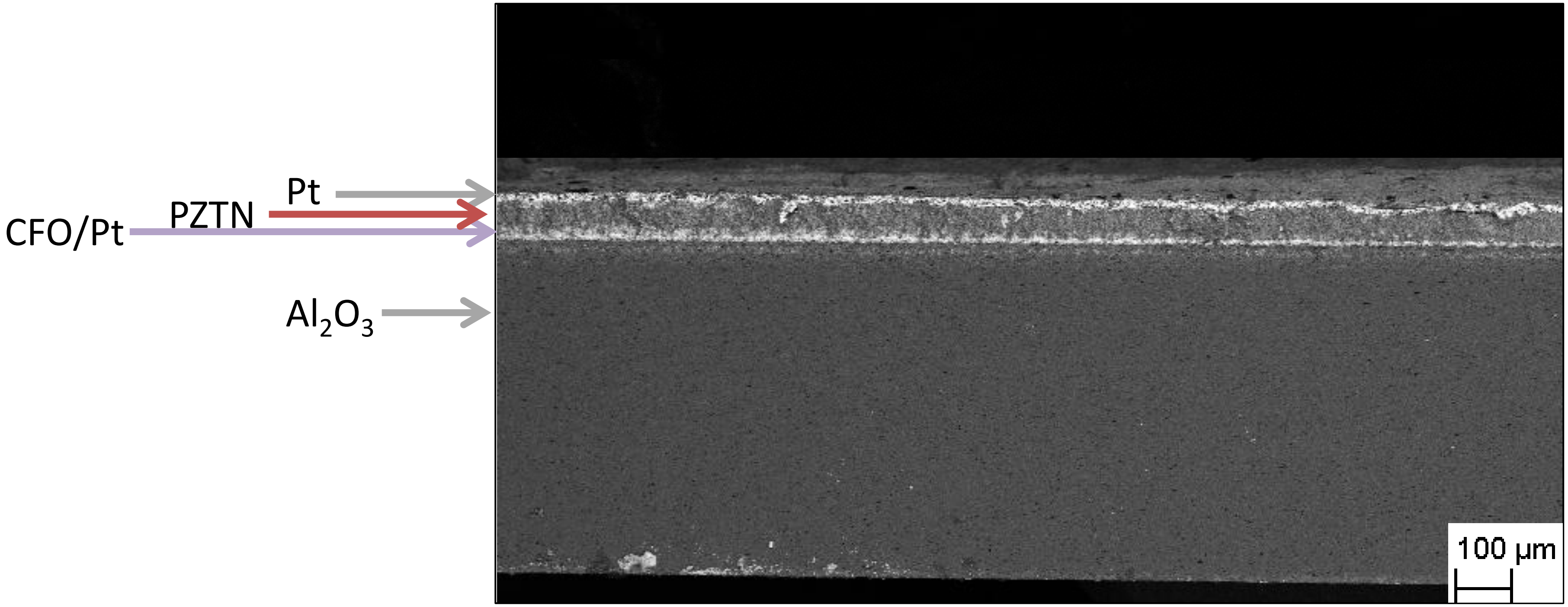
- Single Layer [PZTN]
- Bilayer [PZTN] [CFO]







Conclusion



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Thank you for your kind attention