

Magnetoelectric composite bilayer films by electrophoretic deposition

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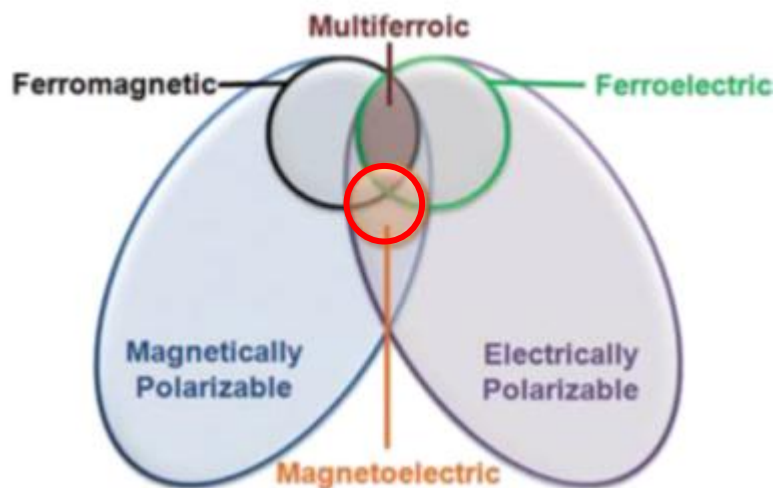
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Magnetoelectric composite bilayer films by electrophoretic deposition

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)



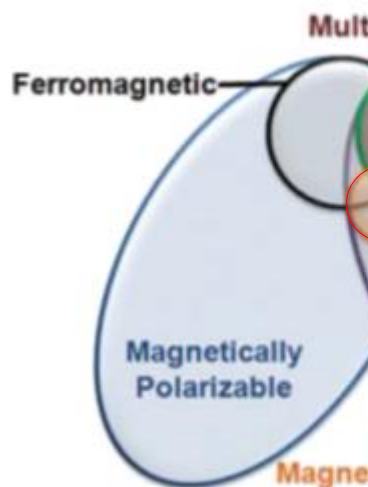
Venn diagram representing the overlap of physical properties in multiferroic materials

G. Schileo Progress in Solid State Chemistry 41, 87-98, 2013

Nan C. V. et Al. Journal of Applied Physics 103, 031101 2008

Magnetoelectric composite bilayer films by electrophoretic deposition

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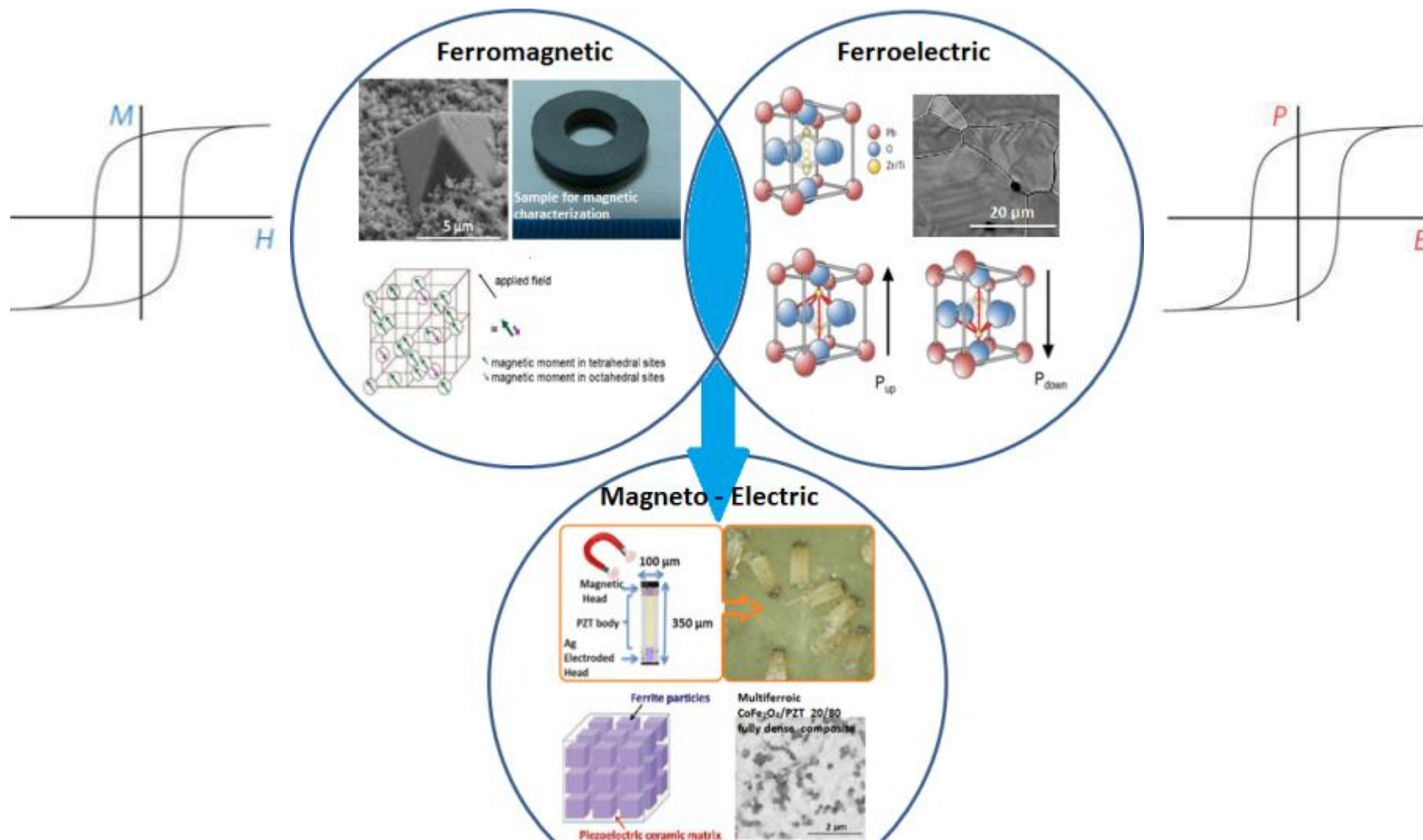
Applications

- 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

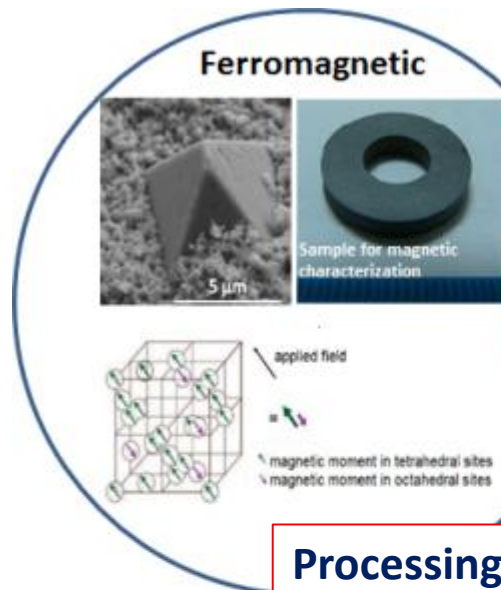
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Magnetoelectric composite bilayer films by electrophoretic deposition



Magnetoelectric composite bilayer films by electrophoretic deposition



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.

Piezoelectric ceramic matrix

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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:

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

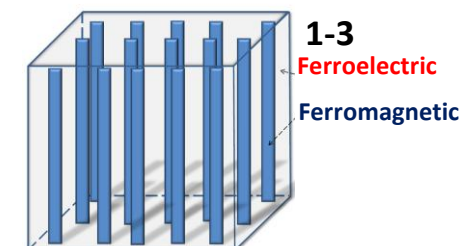
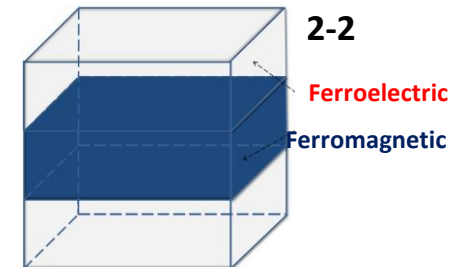
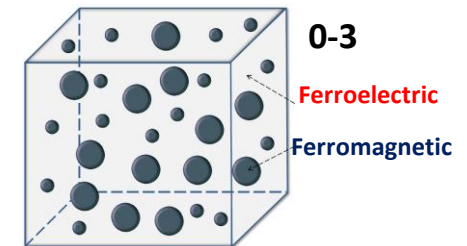
Layout

Single phases

- Ferroelectric
- Ferromagnetic

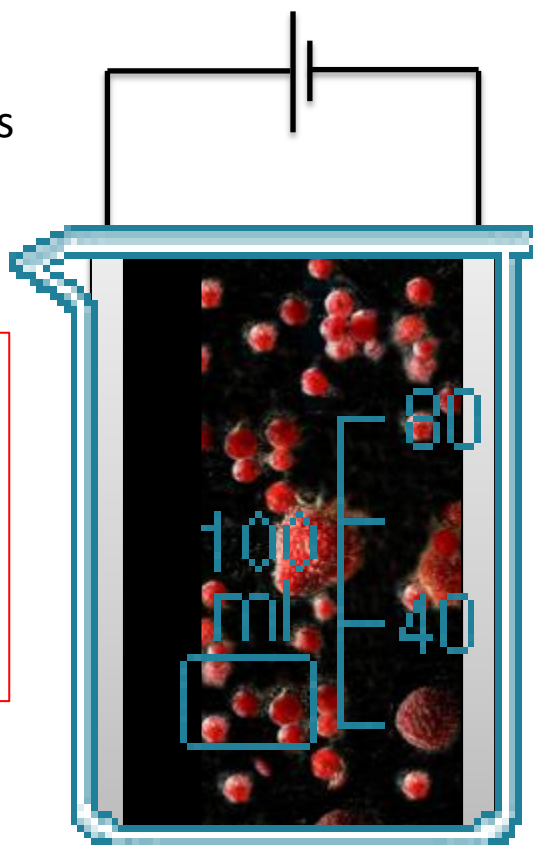
Composites

- Particulate ceramic composites
- Layred ceramic composites



Magnetoelectric composite bilayer films by electrophoretic deposition

- Two conductive electrodes
- Applied electric field



Intrinsic disadvantages

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

Advantages

- Simple apparatus
- Short formation time
- Little restriction of the shape substrate
- High degree of stoichiometry
- Debonding is not required
- Charged powder particles, dispersed or suspended in a liquid medium

Magnetoelectric composite bilayer films by electrophoretic deposition

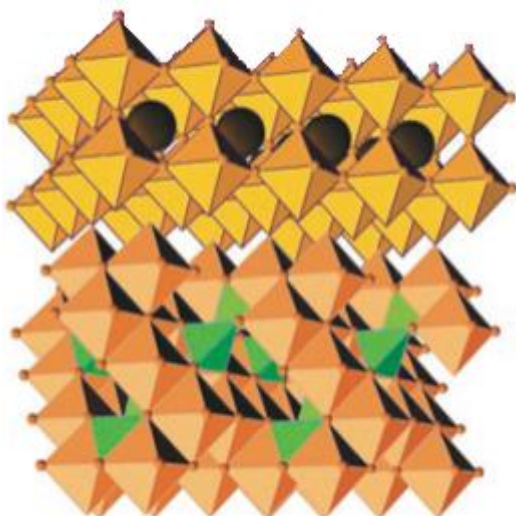
Experimental Work

Heterostructure consisting of bilayer on substrate

- Pt
- $\text{Pb}_{0.988}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.976}\text{Nb}_{0.024}\text{O}_3$
- CoFe_2O_4
- Pt-covered Al_2O_3



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



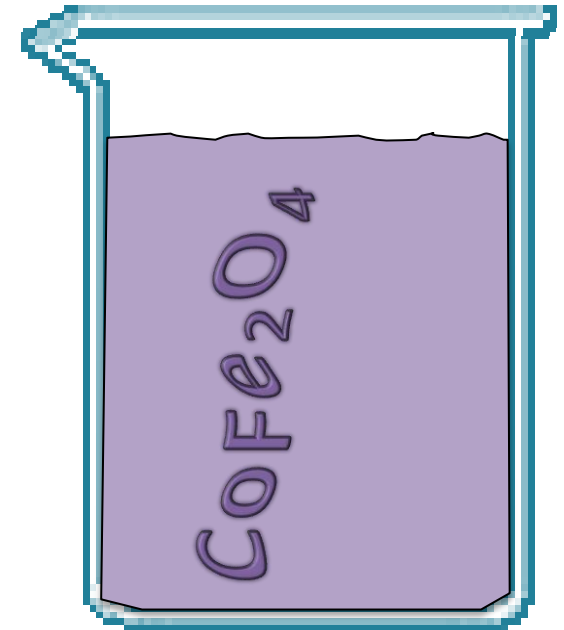
Ferroelectrics crystallize in the **perovskite structure** and it maintain a fraction of the polarisation when the field is removed, after poling

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

Magnetoelectric composite bilayer films by electrophoretic deposition

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

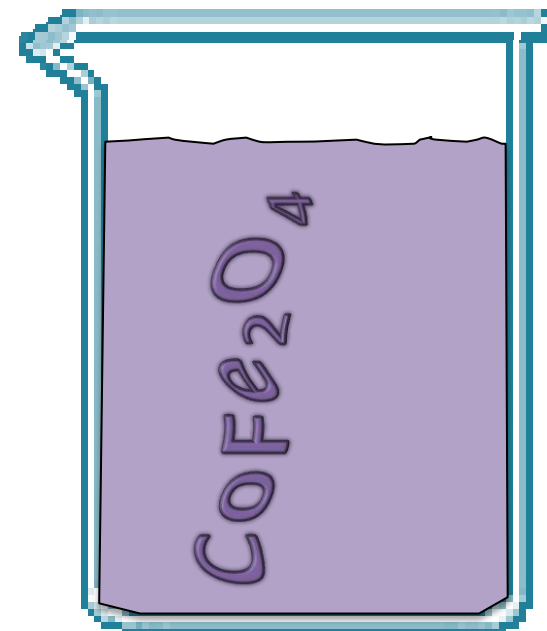


Magnetoelectric composite bilayer films by electrophoretic deposition

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:	$15 \mu\text{S cm}^{-1}$

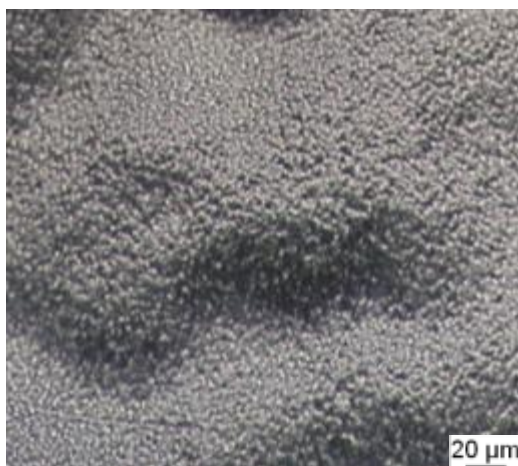


Magnetoelectric composite bilayer films by electrophoretic deposition

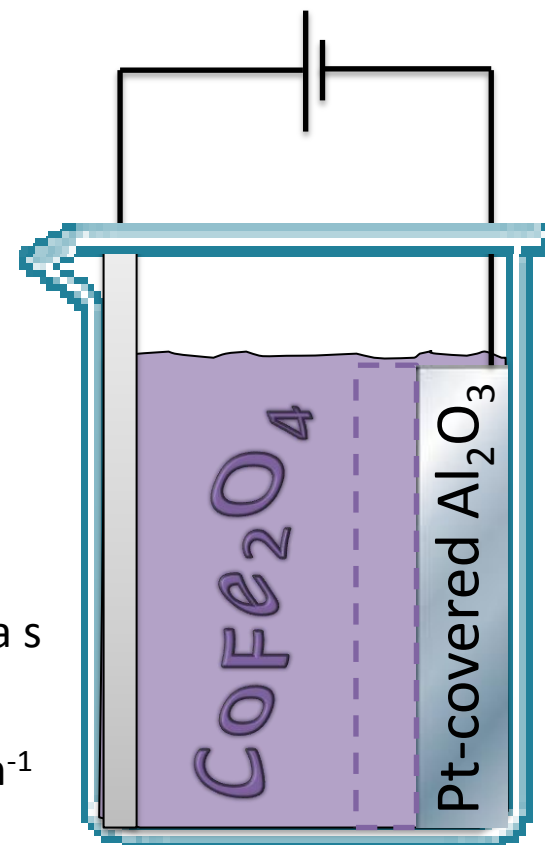
1° EPD Processing

CFO EPD setting:

- plane-parallel cell geometry (1 cm electrodes spacing)
- 20 cm² SS secondary electrode
- 2 cm² Pt-coated alumina working electrode
- 50 cm³ 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
Electrical Conductivity:	15 μS cm ⁻¹

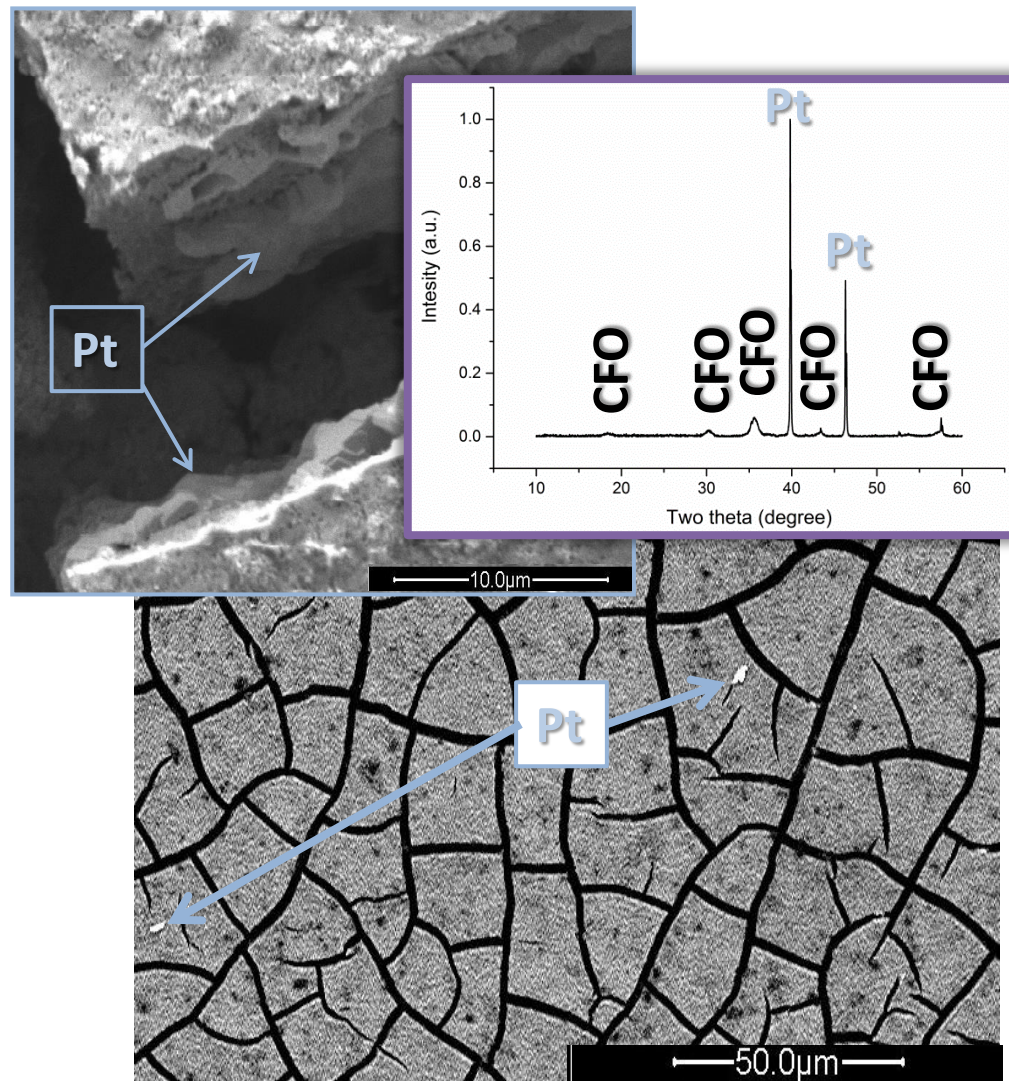
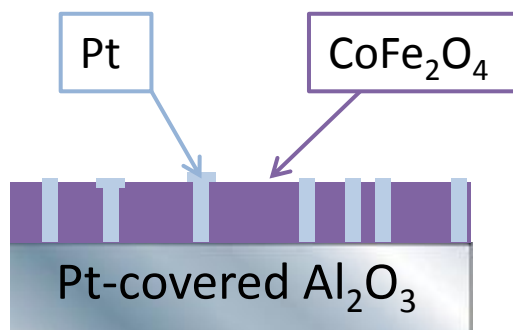


Magnetoelectric composite bilayer films by electrophoretic deposition

Post- 1° EPD Processing

After EPD:

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

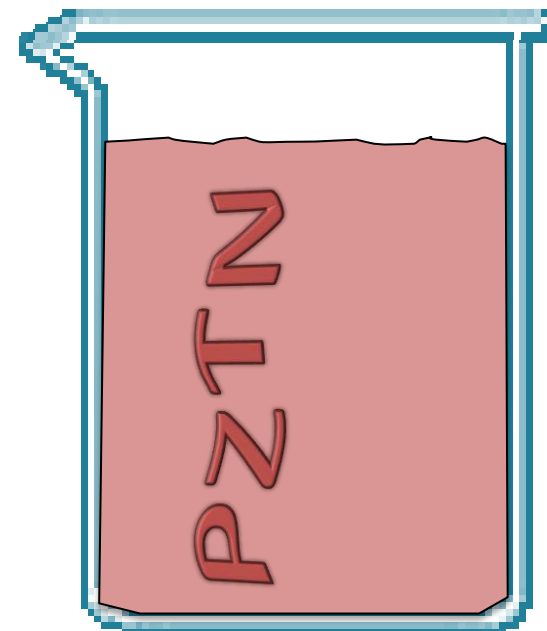
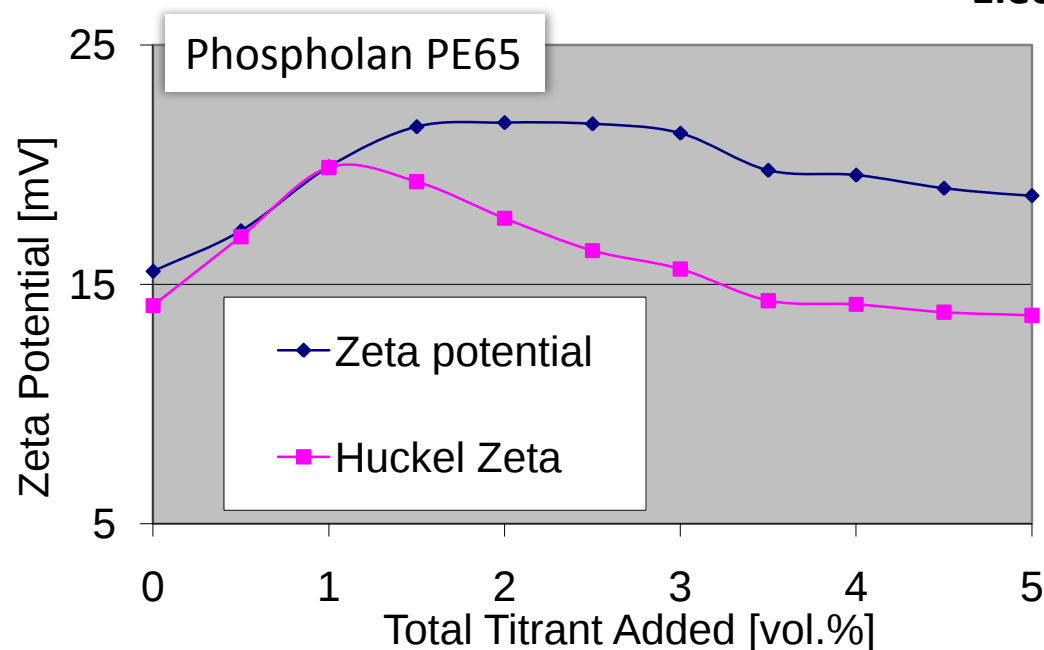


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Before- 2° EPD Processing

- Perovskitic powder
 $\text{Pb}_{0.988}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.976}\text{Nb}_{0.024}\text{O}_3$ 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



Magnetoelectric composite bilayer films by electrophoretic deposition

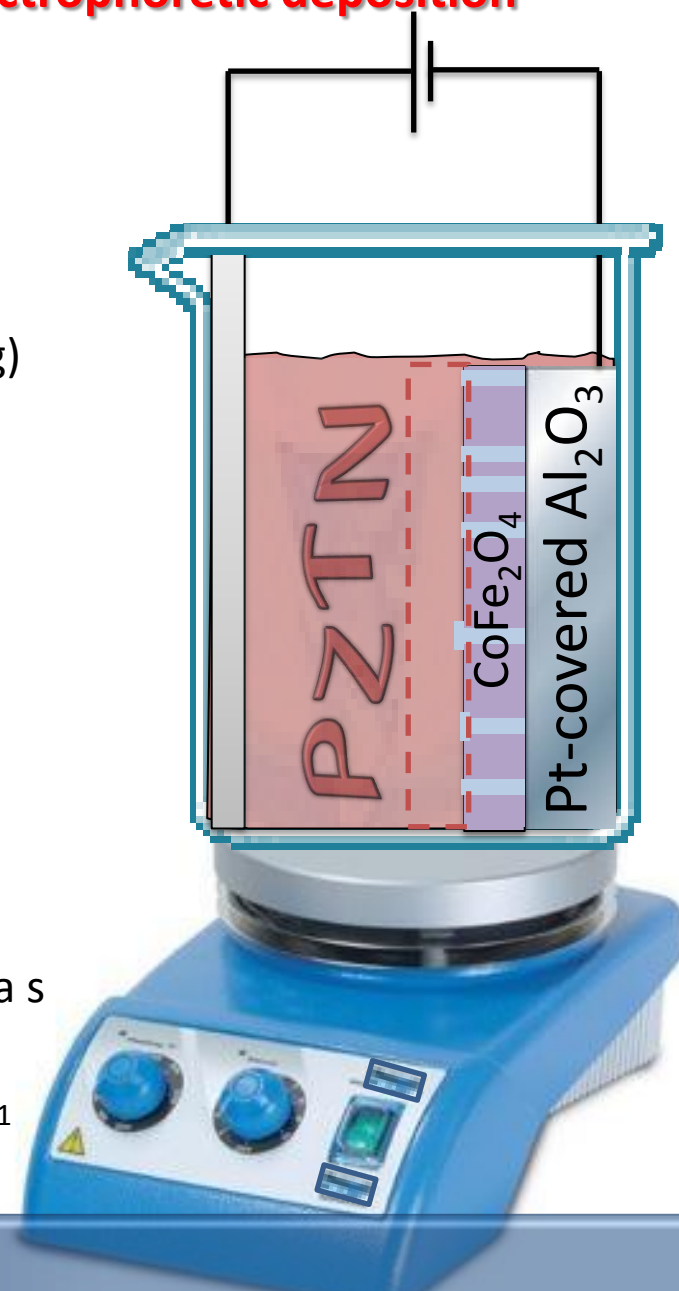
2° EPD Processing

PZTN EPD setting:

- plane-parallel cell geometry (1 cm electrodes spacing)
- 20 cm² SS secondary electrode
- 1.5 cm² Pt-coated alumina working electrode
- 200 cm³ of suspension
- cathodic modality
- constant DC potential at 60 V for 15 s
- Magnetic stirring



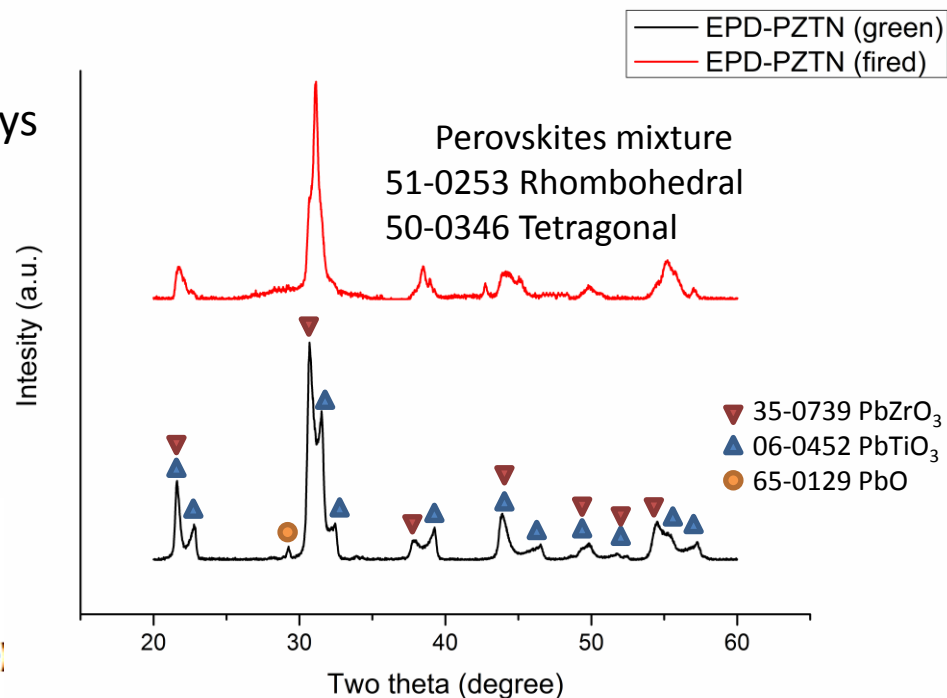
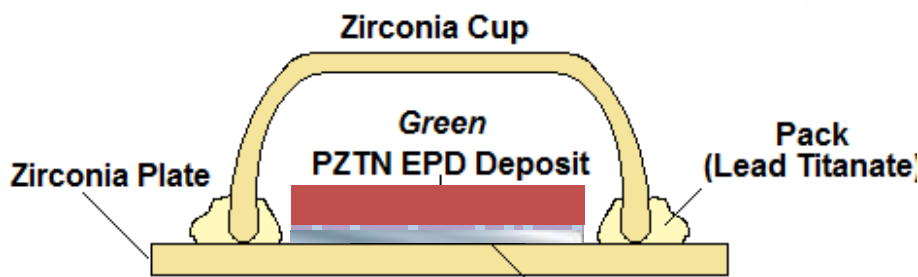
Solid Loading:	15 wt.%
Particle Size (DLS):	185 nm
Viscosity:	1.08 mPa s
ζ-potential :	15.6 mV
Electrical Conductivity:	2 μS cm ⁻¹



Magnetoelectric composite bilayer films by electrophoretic deposition

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

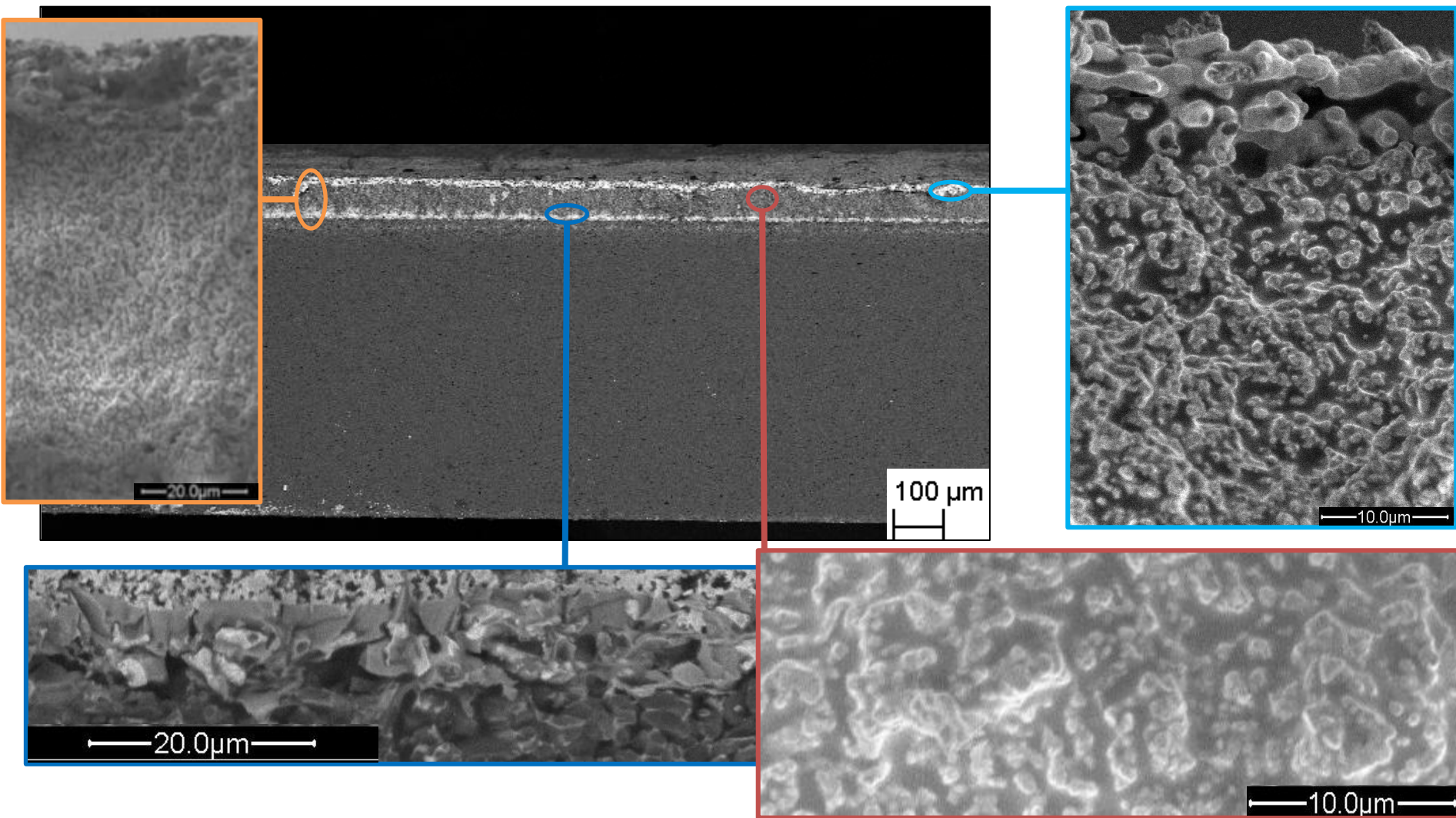


- Pt
- PZTN
- $\text{CoFe}_2\text{O}_4/\text{Pt}$
- Pt-covered Al_2O_3



Magnetoelectric composite bilayer films by electrophoretic deposition

Microstructure

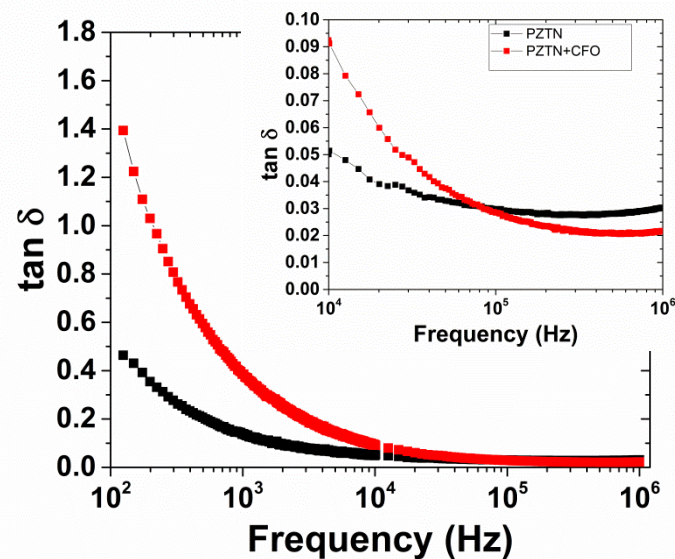
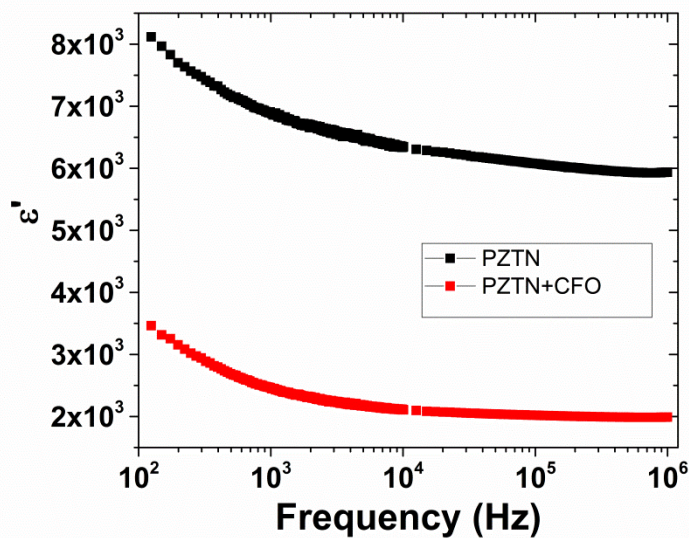
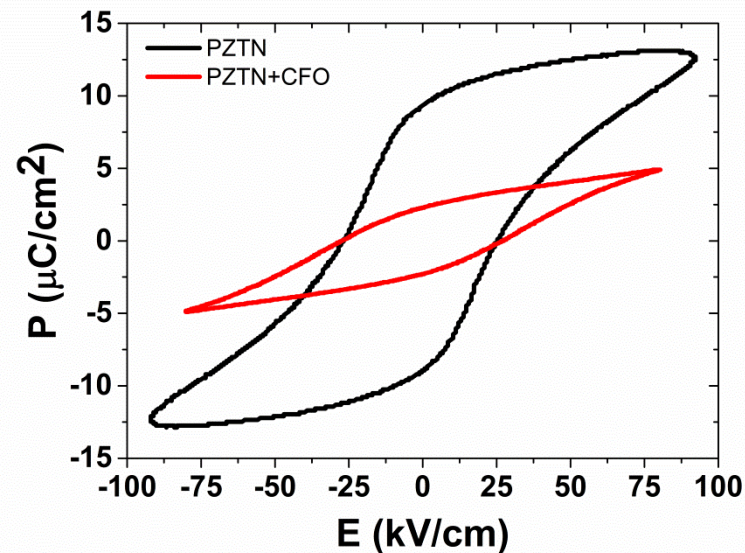


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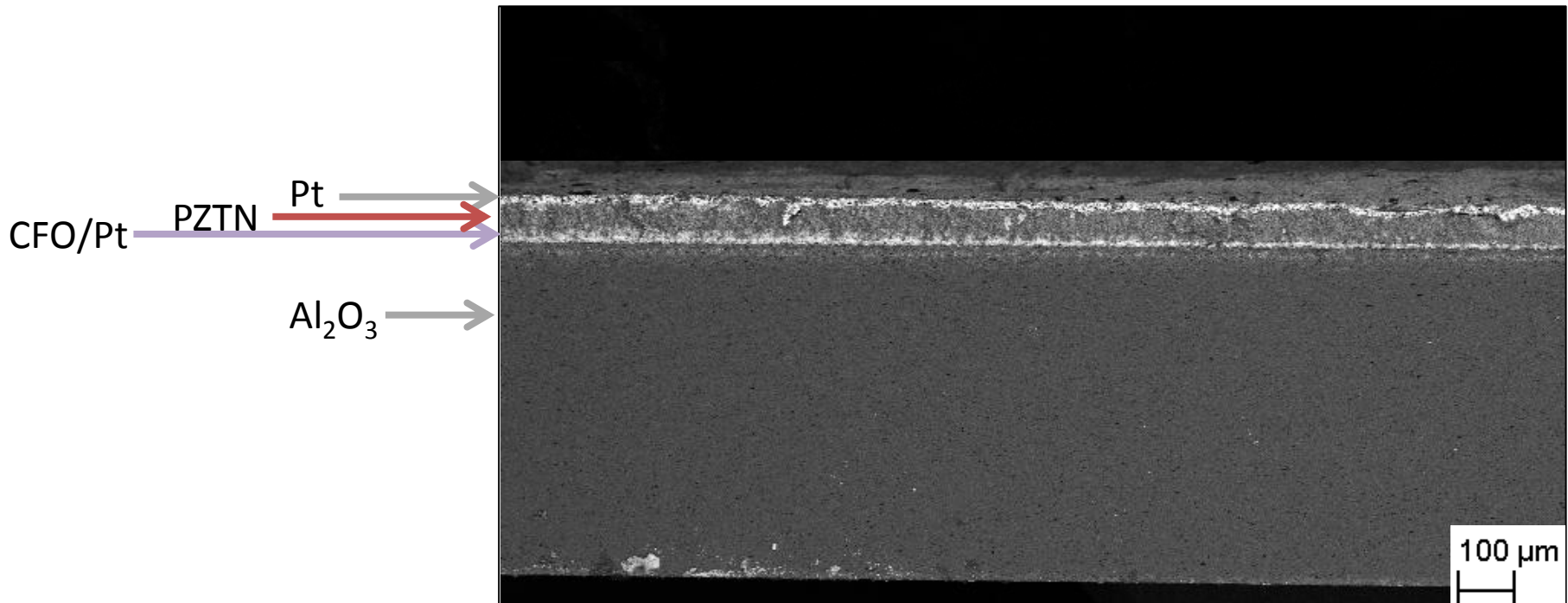
Electric Characterization

— Single Layer [PZTN]

— Bilayer [PZTN] [CFO]



Conclusion



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Thank you for your kind attention

