Magnetoelectric composite bilayer film by electrophoretic deposition

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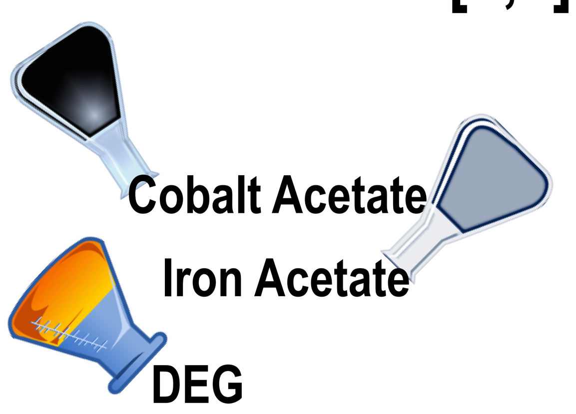
Abstract

In the recent years the interest of the research community towards multiferroic composite materials was growing fast. A number of papers relates to bulk materials while less attention is focused on films. Electrophoretic deposition (EPD) was applied to prepare magnetoelectric (ME) composite bilayer thick films based on perovskite phase and spinel cobalt ferrite as some of the best piezoelectric and magnetostrictive oxides belong these crystal groups. The co-deposition of titanium oxide (TO) and cobalt ferrite (CFO) nanoparticles and the deposition of niobium-doped lead titanate zirconate (PZTN) were made from colloidal suspensions in ethanol keeping constant voltage and recording the current. Good adhesion and compaction of the green film were achieved by optimization of deposition voltage and time while high density of the film and minimized interphase reactions occurred after sintering. The deposited volume, the mixing of dielectric and magnetic phases and the density and ordering of the films have been verified by electron scanning microscopy after heat treatment. No reactions between the different phases was found. The piezoelectric properties were measured on the sintered films.

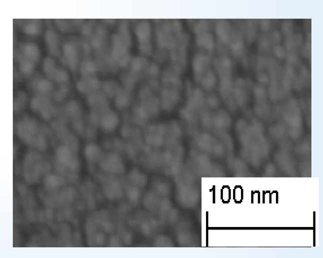
Suspensions

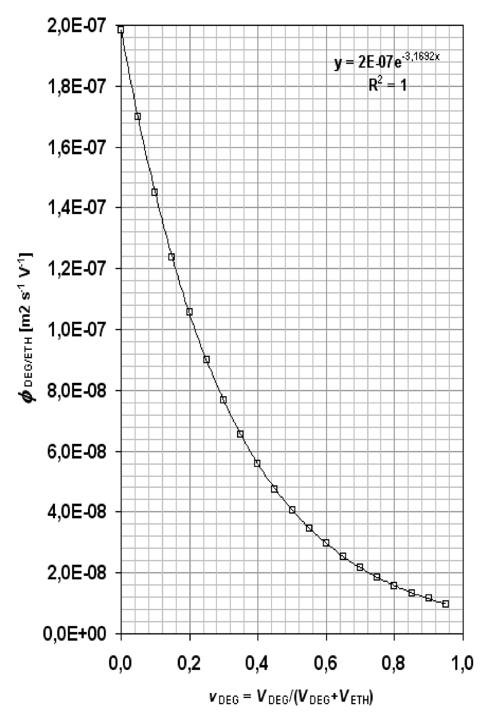
1 - Cobalt Ferrite [1,2]



- Solubilisation at 110°C for 1 h
- Heating to 180°C (2°C/min)
- 3h at 180°C
- Air cooling to RT

Stoichiometry (spinel) :	$CoFe_2O_4$
Particles Density:	5.27 g cm^{-3}
Suspension Density:	1.23 g cm^{-3}
Solid Loading, wt%:	12.9
Particle Size (DLS):	7.1 nm
Viscosity:	56.7 mPa s
ζ-potential :	47.5 mV
Electrical Conductivity:	15 µS cm^{-1}





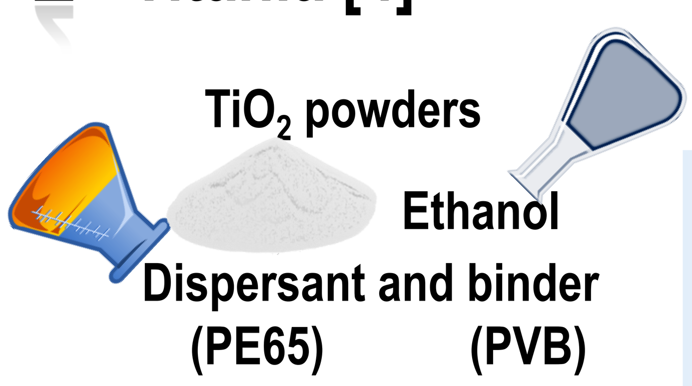
Dilution with ethanol [3]

Reduced viscosity of the mixed DEG/ethanol medium increase particle flux by increasing the mobility per unit ζ-potential (figure of merit, Φ) and give beneficial effects on film coagulation.

$$\mu = \frac{2}{3}\frac{\zeta \cdot \varepsilon}{\eta}$$

$$\varphi = \frac{\varepsilon}{\eta} = \frac{3}{2}\cdot\frac{\mu}{\zeta}$$

2 - Titania [4]



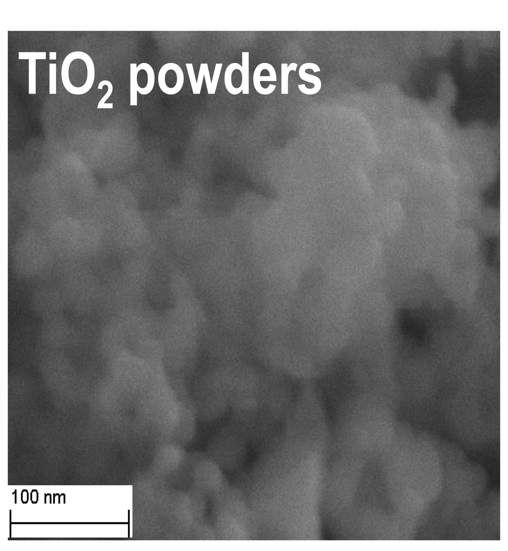
- Ball milling and stirring

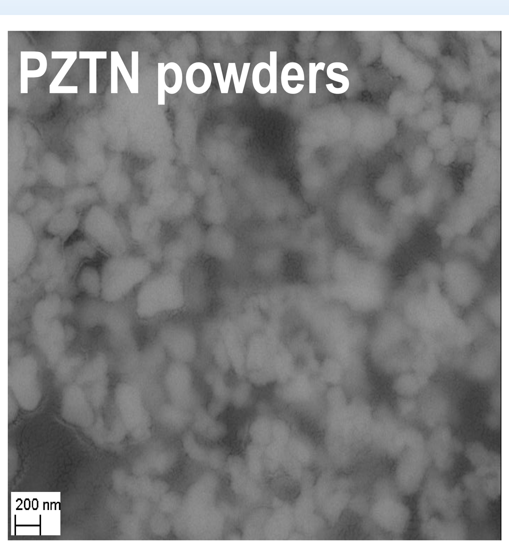
Particles Stoichiometry:	TiO_2 (Degussa P25)
Suspension Density:	0.88 g/cm^{-3}
Solid Loading, wt%:	11.4
Particle Size (DLS):	26 nm

3 - Lead zirconate titanate [5,6]

- Ball milling and stirring

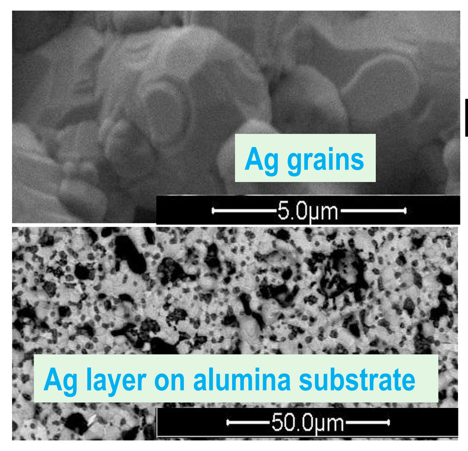
Particles Stoichiometry:	$Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$
Suspension Density:	0.88 g/cm^{-3}
Solid Loading, wt%:	11.3
Particle Size (DLS):	145 nm





Necessary conditions for two-steps EPD process: substrate and first deposited film must be conductive!

Substrate

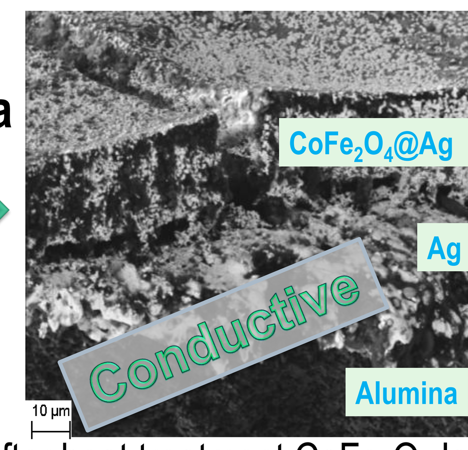


Ag-coated alumina

EPD-CFO film on Ag-coated alumina

Firing at 500°C x 1h

First deposited film

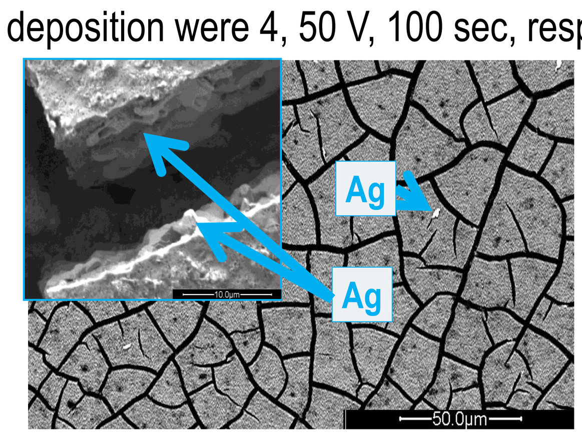


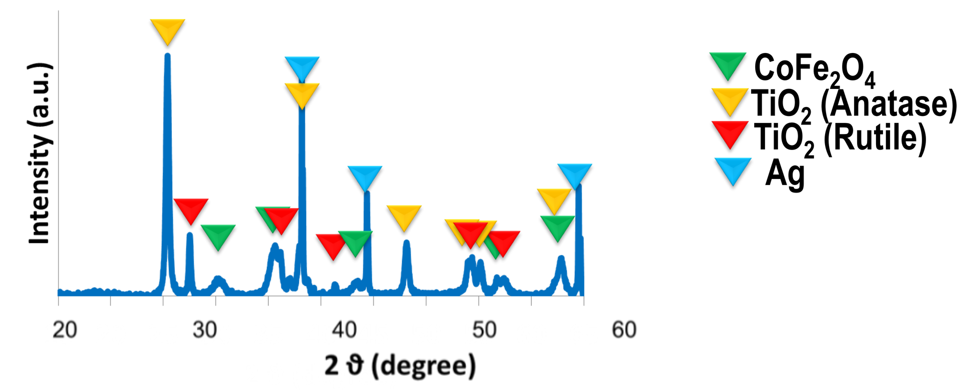
After heat treatment $CoFe_2O_4$ layer resulted embedded in silver

EPD

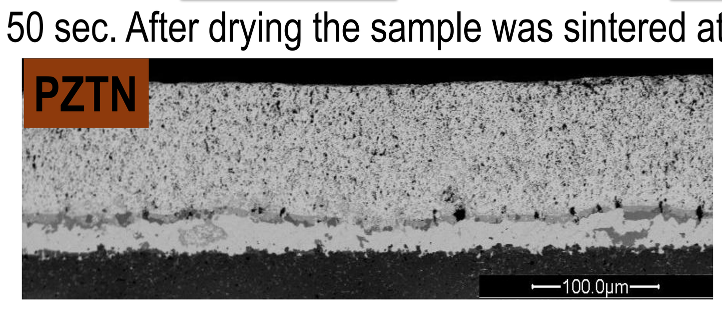
EPD tests were performed in a plane-parallel cell geometry (1 cm electrodes spacing) and setting cathodic modality with constant DC potential up to 60 V vs. a 20 cm^2 SS secondary electrode.

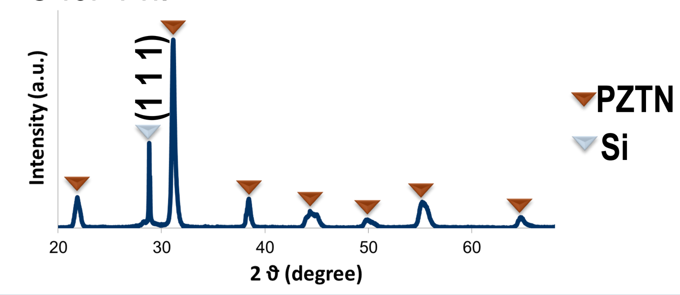
First EPD-CFO/TiO_2 film on Ag-coated alumina: a suspension obtained by mixing the cobalt ferrite suspension with the titania one was deposited. CFO/TiO_2 weight ratio of suspension, voltage and time deposition were 4, 50 V, 100 sec, respectively. After drying the sample was fired at 500 °C for 15 min.



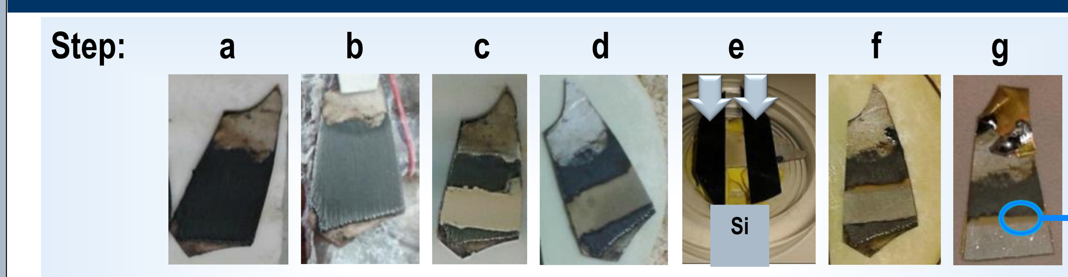


Second EPD-PZTN film on first EPD-CFO/TiO_2: PZTN suspension was deposited under 30 V for 50 sec. After drying the sample was sintered at 800 °C for 1 h.





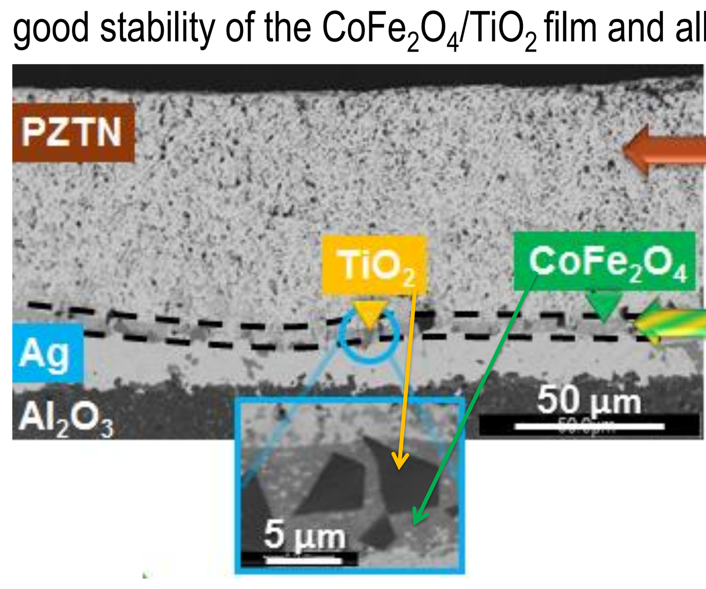
Process

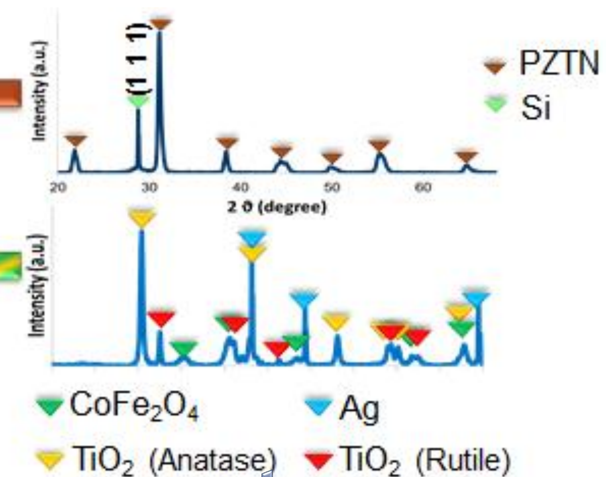


(a) CFO/TiO_2 co-deposition
(b) Drying, sintering and XRD analysis
(c) PZTN deposition
(d) Drying and sintering
(e) XRD analysis
(f) Metallization
(g) Poling

Results

Although cracking occurs during drying in air, a pre-sintering heat treatment in the range of 400-500 °C gives a good stability of the $CoFe_2O_4$/TiO_2 film and allows the Ag wetting of the cracks.





PZTN layer
Relative density: 95%

CFO/TiO_2 layer
Relative density: 98%
25 vol% TiO_2
75 vol% CFO

Conclusions

- Magnetoelectric composite bilayer film on Ag-coated alumina was produced
- The microstructure analysis was performed by SEM/EDS and XRD
- Piezoelectric activity was tested

Piezoelectric properties!

References

[1] G. Baldi et al., J. Magn Magn Mater 311 (2007) 10-16
[2] D. Gardini et al., J Nanosci Nanotechnol 8 (2008) 1979-1988
[3] C. Baldisserri et al. Key Eng Mat, 507 (2012) 85-88
[4] C. Baldisserri et al. J Colloid Interface Sci, 347 (2010) 102–111
[5] C. Baldisserri et al. Sensor Actuat A-Phys 174 (2012) 123-132
[6] C. Galassi et al. J Eur Ceram Soc, 17 (1997) 367–371

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