PhD topic: "Multilayered antiferroelectric supercapacitors for green and efficient energy storage: fundamental study for real-life applications"

Doctoral School: « Interfaces » / **Topic:** Solid-state Physics
Lab: Structures, Properties and Modelling of Solids (SPMS)
Thesis supervisor: Pierre-Eymeric JANOLIN / co-supervisor **Cosme MILESI-BRAULT**
Starting date: 1st October 2025 / Application deadline (at 23:59): 30th April 2025

Keywords: ferroelectrics, material synthesis, energy storage

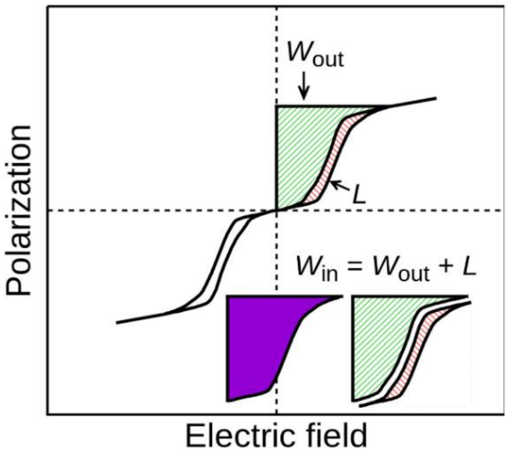
Topics: solid-state physics, ferroelectrics, material synthesis through chemical and physical deposition techniques, material characterisation: x-ray diffraction, electronic microscopy, atomic force microscopy, electrical measurements, spectroscopy…

Supervision: This thesis work will be co-supervised by Cosme Milesi-Brault, maître de conférences (expertise on synthesis and spectroscopy of ferroelectrics) and Prof. Pierre-Eymeric Janolin (expertise on structural and electrical properties of ferroics).

Quick summary of the thesis project:

Antiferroelectrics are dielectric materials composed of an antipolar array of dipoles, which display no macroscopic polarisation. They can be switched to a polar ferroelectric phase by application of an electric field: this field-induced phase transition is called switching, which induces a so-called "double hysteresis loop" in its polarisation vs electric field curve. The shape of this double hysteresis loop allows for efficient storage of electrical energy and a very fast discharge, useful for high-power applications [1, 2].

In particular, the development of sustainable alternatives to traditional lead-based ferroelectrics and antiferroelectrics is a crucial step towards creating environmentally friendly energy storage solutions.



Principle of energy storage in antiferroelectric materials. W_{in}, W_{out} and L respectively indicate the energy density needed to charge the antiferroelectric capacitor, the recoverable energy density and losses. Adapted from Ref. [5].

On a more fundamental side, layering antiferroelectric and ferroelectric materials could also induce extremely rich topological physics, such as ferroelectric skyrmions [3, 4], which could be further energy storage properties of multilayers [5, 6, 7], but also in other applications (e.g. extremely low-power computing). Investigating how such antiferro/ferroelectric multilayers behave under an electric field (including the underlying mechanisms of electric field-induced phase transitions) is also a very important topic in the ferroic community.

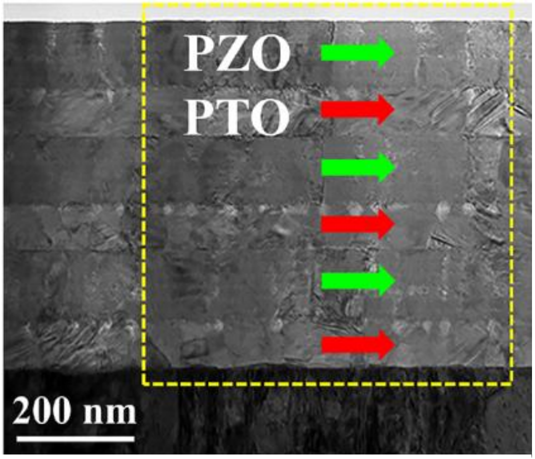
This PhD research project will focus on the synthesis and characterization of novel materials that can replace toxic lead-based compounds in energy storage devices, such as supercapacitors.

Materials of interest are lead-free inorganic perovskites such as $NaNbO_3$, $AgNbO_3$, $BiFeO_3$, $(Nb_{0.5}Bi_{0.5})TiO_3$, which are (anti)ferroelectric materials.

During this PhD, the candidate will:

- Design and synthesise eco-friendly alternatives to standard lead-based (anti)ferroelectrics in the shape of multilayers
- Analyse in-depth the electrical, structural, and chemical properties of these multilayers
- Investigate the suitability of these materials for energy storage devices, particularly supercapacitors, and optimise their performance for enhanced energy density and power density.
- Study *in-situ* (anti)ferroelectric multilayers under the influence of electric fields and temperature change to elucidate their underlying mechanisms of their phase transitions

The first step of this PhD project is to **synthesise lead-free antiferroelectric multilayers** [7] by chemical solution deposition (CSD) and pulsed laser deposition (PLD) and to **optimise their density of storable energy**. The second step of this project is to **shed light on the electric-field induced switching mechanisms of these multilayers** to further improve our knowledge of these materials.



SEM cross-section image of a multilayer capacitor made by CSD. Adapted from [7].

Main experimental techniques:
Chemical solution deposition (CSD) and pulsed laser deposition (PLD) for depositing multilayer thin film materials; x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) for (micro)structural characterisation; x-ray photoelectron spectroscopy (XPS), electron diffraction spectroscopy (EDS) for chemical analysis; electrical measurements (polarisation, capacitance, permittivity).

Bibliography:

[1] B. Xu, J. Íñiguez, and L. Bellaiche, 'Designing lead-free antiferroelectrics for energy storage', Nat Commun, vol. 8 (2017)
[2] Z. Liu et al., 'Antiferroelectrics for Energy Storage Applications: a Review', Adv Mater Technol, vol. 3, no. 9, p. 1800111 (2018)
[3] Yadav, A. K. et al., Observation of polar vortices in oxide superlattices. Nature 530, 198–201 (2016).
[4] Das, S. et al., Observation of room-temperature polar skyrmions. Nature 568, 368–372 (2019).
[5] H. Aramberri, N. S. Fedorova, and J. Iniguez, 'Ferroelectric/paraelectric superlattices for energy storage', Sci Adv, vol. 8, no. 31, p. 4880 (2022)
[6] T. Zhang et al., 'Superior Energy Storage Performance in Antiferroelectric Epitaxial Thin Films via Structural Heterogeneity and Orientation Control', Adv Funct Mater, vol. 34, no. 4, p. 2311160 (2024)
[7] Y. Zhang et al., 'High Energy Storage Performance of PZO/PTO Multilayers via Interface Engineering', ACS Appl Mater Interfaces, vol. 15, no. 5, pp. 7157–7164 (2023)

If you are interested, please quickly contact cosme.milesi-brault@centralesupelec.fr