SPMS, UMR CNRS 8580

LABORATORY STRUCTURES, PROPERTIES AND MODELING OF SOLIDS

Structures
Properties
Modeling of
Solids

THEMATIC FIELDS

ADVANCED FERROICS

Ferroic materials are multifunctional materials whose principle is based on controlling a ferroic parameter (electric polarization, magnetization, elastic strain) by an external stimulus (electric and magnetic fields, light, temperature, etc.). There are many applications in health (ultrasound probes), electronics and digital (FeRAM, FeFET transistors, synapses for neuromorphic computing), automotive (pressure sensors for airbag triggers), and defense (sonar). The ferroelectric theme will build on the strengths of the SPMS and the momentum created by the results of recent calls for projects (joint laboratory with the SME Pytheas, European TSAR project, ANR projects) to strengthen itself and develop new research areas:

- **New actuators**: supported by the creation of the joint laboratory SPyMS between SPMS and the company Pytheas, the ANR MEGAFILM, and an Astrid project, the ferroic axis will develop the piezoelectric and electrostrictive materials of tomorrow.
- **Topological objects and ferroelectric nanostructures**: the ferroelectric axis develops means for synthesis and advanced characterization (X-ray diffraction, STEM, spectroscopies) of ferroelectric nanostructures (nanoparticles, superlattices). The objective is to discover exotic polarization textures (vortexes, skyrmions) with original topological properties for applications in electronics (negative capacitance), health (sensors), and the environment (photocatalysis). The FET Open TSAR, the ANR UFO and TATTOO support this research.
- **Photo-induced effects in multiferroics**: supported by the ANR SUPERSPIN and THz-Mufins, the ferroic axis seeks to understand the properties of multiferroics under illumination: photovoltaics, photocatalysis, photo-induced spin currents, and deformations generated under lighting.

DEFECTS AND NON-EQUILIBRIUM MATERIALS

Defect control is the central part of materials engineering. The control of defects applies essentially to oxide materials where the composition will have a direct influence on a concrete functional property: protonic conduction, transport properties in nuclear fuels, dielectric constant, piezoelectricity, electrostriction...

The aim of this thematic field is to

- understand how substitutions can modify the behaviour of the target material,
- study the influence of the environment (atmosphere, temperature) on the evolution of the properties of a system in operation.
- look at how a specific preparation of a material can alter its properties and keep them out of equilibrium in the device's operating conditions.

Such an understanding classically requires a combination of structural characterizations (XRD, Raman, STEM...), modeling by ab initio calculation or derived methods, and electrical measurements allowing to separate the different contributions (composition, microstructure, environment) to the physical properties.

Our main objectives in this area are to:

- **accelerating the development of materials** to reach a sufficient knowledge of the effect of a given dopant on the properties. This requires the implementation of new experimental tools allowing for scanning a large number of compositions in a much shorter time. The analysis and calculation methods must evolve to analyze a large number of data and extract the relevant information using AI-type approaches.
- **strengthen the understanding of defects' effect** through techniques/modelling to understand long and shortrange order simultaneously. The aim is to strengthen the panel of tools available to have a complete picture possible of mechanisms operating at different scales and allowing explaining most of the observed properties.

Application Domains

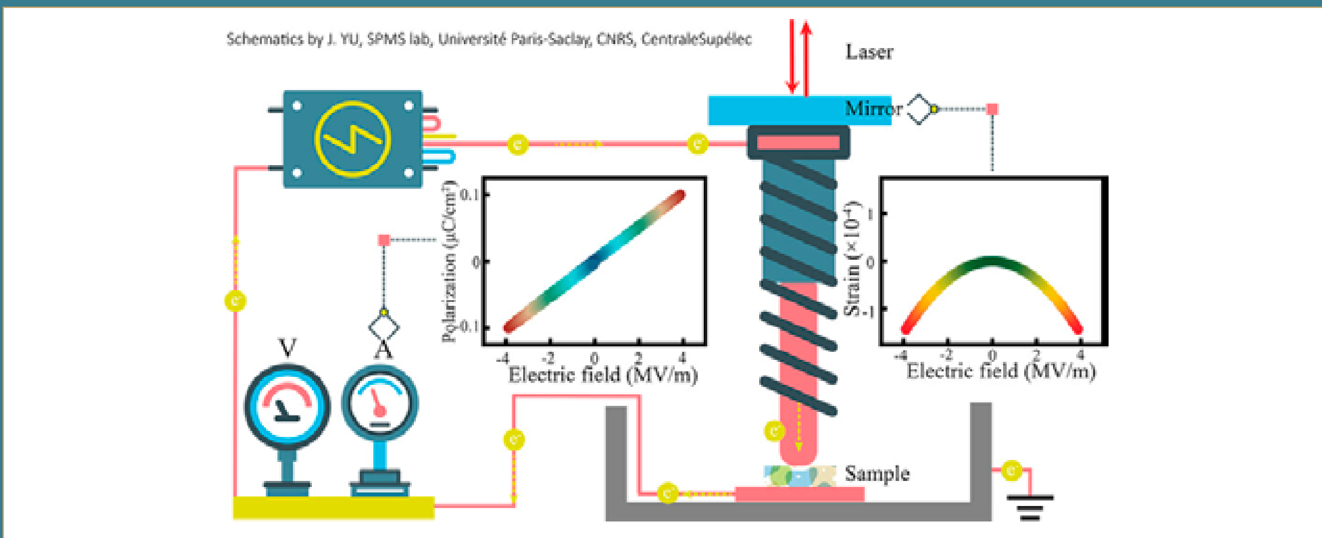
Electronic, Energy, Environment and Pharmaceutical industries, functional materials, piezoelectric transducers, energy harvesters, solid oxide fuel cells, multilayer capacitors, electrostrictive actuators, memories and artificial synapses, quantum enabling technologies, photovoltaic cells, photo- and piezo-catalysts, photo-sensors and emitters, biomedical field, hydrogen technologies, nanostructured ceramics, nuclear materials.

HIGHLIGHTS 2022

Creation of the SPyMS

Launch of the ANR-funded, CNRS joint laboratory, SPyMS, between SPMS and the company Pytheas (founded by Frédéric Mosca, ECP2005). The joint laboratory is dedicated to the development, fabrication, characterisation, and analysis of tomorrow's electroactive materials and is directed by Pierre-Eymeric Janolin, Professor at CentraleSupélec.

EXAMPLES OF STUDIES

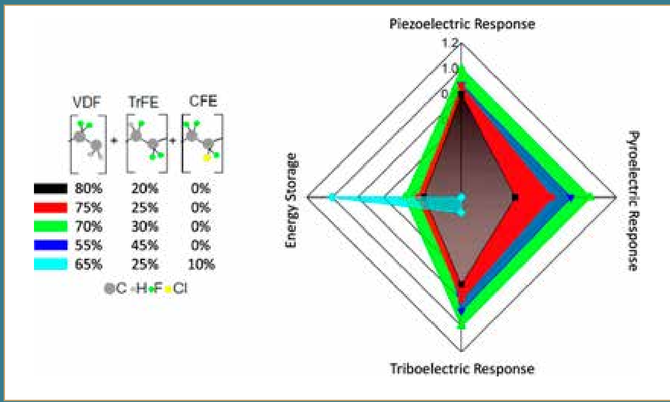


Giant electrostrictors: a novel paradigm for electro-actuation

Piezoelectricity is the electromechanical coupling at the heart of most actuator and sensing applications driven by an electric feld. However, the material of choice for applications is the PZT that contains lead. For environmental and regulatory reasons, alternatives must be found. If some lead-free piezoelectrics match some of PZT's performance, they fail to shift the industry's practice. Electrostrictors is another electromechanical coupling that has been brought back to attention with the discovery of "giant electrostrictors" with performances several orders of magnitude larger than expected. An understanding of the underlying mechanism is paramount to the further exacerbation of this property. We have put forward a defnition of what "giant electrostriction" is [1], set up a methodology to calculate electrostriction from ab initio [2], shown that the response can be made as large as desired in thin flms [3], and discovered through a data-mining approach coupled with numerical simulations that many more superior electrostrictors exist [4].

[1] J. Yu, P.E. Janolin, J.Appl.Phys., 131 170701 (2022), selected as "featured" review and SciLight (doi: 10.1063/10.0010487)
[2] D. Bennet, DSP Tanner, Ph Ghosez, PE Janolin, E Bousquet, Phys.Rev.B 106, 174105 (2022)
[3] DSP Tanner, PE Janolin, E Bousquet Phys.Rev.B 106, L060102 (2022)
[4] DP Trujillo, A. Gurung, J. Yu, SK. Nayak, SP Alpay, PE Janolin, npj Comp. Mat. 8, 251 (2022)

From energy harvesting to energy storage using PVDF-based ferroelectric polymers

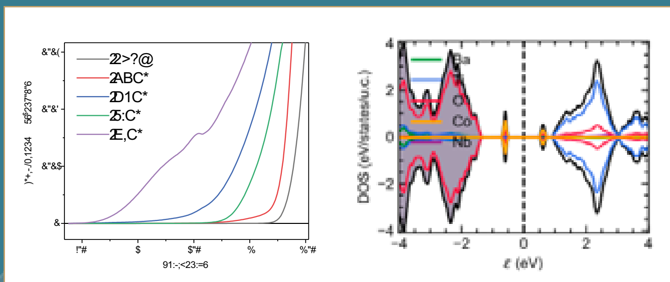


Ferroelectrics and their energy conversion ability are utterly crucial for various applications in modern electronics. In recent years, the need to develop flexible electronics has emerged due to the increased popularity of body-worn devices in all aspects of our life. This raised the need for materials enabling energy harvesting and storage and being flexible, scalable, withstanding wear and temperature variations, and chemically resistant and biocompa-tible. Here, we applied the well-established material's figures of merit to five polyvinylidene-fluoride (PVDF)-based polymers ranging from ferroelectric to relaxor-like behavior to emphasize the importance of several key material parameters contributing to the maximal power output of energy harvesting devices. Most specifically, we studied the energy harvesting through piezoelectric, triboelectric, and pyroelectric methods, where electric charges are produced from mechanical stresses, contact between two surfaces, i.e. electrostatic induction, and temperature variations, respectively. We also discussed the possibility of the same functional material storing the output energy for the development of scalable multifunctional devices.

[1] M. Fricaudet, K. Ziberna, S. Salmanov, J. Kreisel, D. He, B. Dkhil, T. Rojac, M. Otoničar, P.E. Janolin, A. Bradeško**, ACS Appl. Electron. Mater. 4, 5429 (2022)*
**SPMS PhD student, **SPMS Post-doc student*

Co-doping strategy in ferroelectrics for improving photovoltaic performances

Unlike conventional semiconductor p–n junctions, the so-called bulk photovoltaic (PV) effect in ferroelectric materials can generate voltages larger than the bandgap. Moreover, new functionalities related to the coupling between the ferroelectric polarization and the PV effect are conceivable. Unfortunately, most ferroelectrics suffer from a large bandgap, typically larger than 3 eV. This results in poor absorption of the solar spectrum, causing low energy conversion efficiency in most ferroelectric-based solar cells. By combining experimental and theoretical tools, we reveal by using a co-doping strategy on the model BaTiO3 (BTO) ferroelectric material, that while the electronic bandgap is weakly changed, if any, the unfilled d-orbital states of dopants introduce extra bands within this bandgap that help absorb light below the bandgap by pushing down the onset of absorption to 1.5 eV, significantly improving the PV performances. In contrast, at the same time, good ferroelectric and piezoelectric properties are maintained, envisioning more than PV applications.

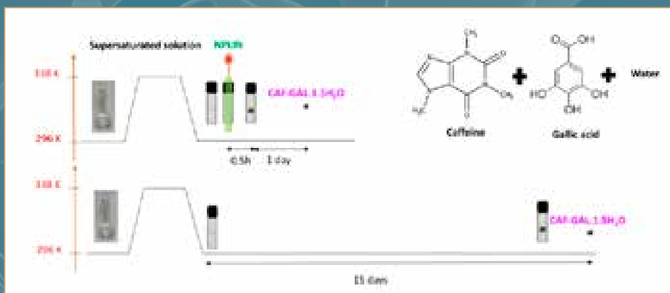


Left: *Absorption vs energy, showing the onset of absorption is significantly decreased compared to pure BTO,* **Right**: *Density of States vs energy, revealing extra states due to dopants within the bandgap of BTO.*

[2] S. Hao, M. Yao*, G. Vitali-Derrien*, P. Gemeiner, M. Otoničar, P. Ruello, H. Bouyanff, P.E. Janolin, B. Dkhil, C. Paillard, J. Mater. Chem. C 10, 227 (2022)*
**SPMS PhD student*

Laser-induced co-crystallization for pharmaceutical industry

For the first time, we have been able to laser-induce a co-crystallization. Hence, caffeine (CAF) - and gallic acid (GAL) in water give co-crystals [1] using the Non-Photochemical Laser-Induced Nucleation (NPLIN) technique [2-4]. The nucleation temporal control of NPLIN and the induction time reduction (70 times shorter than spontaneous nucleation) allow the obtention of cocrystals on-demand, with excellent repeatability. Supersaturated solutions are exposed to a 532 nm wavelength nanosecond pulsed laser at 296 K. Crystalline form characterization combines Raman scattering, high-performance liquid chromatography, thermogravimetry, differential scanning calorimetry, and powder X-ray diffraction. Two different cocrystal forms are obtained: a new polymorph of hemihydrate CAFGAL$_{0.5}$H$_2$O and a new hydrate form CAFGAL$_{1.5}$H$_2$O. These results open a promising way to crystallize cocrystals in the context of the pharmaceutical industry.



Laser-induced co-crystallization of caffeine and gallic acid in water [1].

[1] Mellah, D.; Nicolai, B.; Fournier, B.; Bošnjaković-Pavlović, N.; Legrand, F.X.; Gemeiner, P.; Boemare, V.; Nicolas Guiblin, N.; Assi, A.; Tfayli, A.; Konate, S.; Durand, P.; Spasojević-de Biré A. New Cocrystallization Method: Non-photochemical Laser-Induced Nucleation of a Cocrystal of Caffeine–Gallic Acid in Water Cryst. Growth Des. 2022, 22, (10) 5982–95. https://doi.org/10.1021/acs.cgd.2c00624.*
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Industrial Partners

- COORSTEK
- EXXELIA
- FERROPERM
- HORIBA-JOBIN YVON
- IMASONIC
- IXSEA (SONAR)
- LETI
- NANOE
- PYTHEAS TECHNOLOGY
- SAINT-GOBAIN
- SCHLUMBERGER
- ST MICROELECTRONICS
- SRT Microcéramique
- THALES & THALES UNDERWATER SYSTEMS

Academic Partners

NATIONAL: CEA-Saclay, CEA-DAM, CEA-Cadarache, École Polytechnique, Faculty of Pharmacy (Paris-Saclay), University Paris XI, University Paris VI, ICMCB, ILL, ESRF, LLB, SOLEIL, LETI, THIAIS, VITRY, ENS-ParisSaclay, C2N-Saclay, UMPhy-Saclay, GEMAC-Versailles, GREMAN-Tours, IMMM-Le Mans, UPJV-Amiens, etc.

INTERNATIONAL: University of Tokyo Waseda, Spring8, University of Arkansas, EPFL, University of Cracaw, University of Belgrade, University of Barcelona, Georgia Tech, JSI-Slovenia, Univ. Duisburg-Essen-Germany, LIST&Univ-Luxembourg, Univ. Liège-Belgium, UCLondon-UK, ISIS-UK, NTNU-Norway, Univ. Tunis El Manar-Tunisia, Xi'an Jiatong Univ-China, East China Normal Univ.-China, SITP-Shanghai-China, UDrexel-USA, UC Berkeley-USA, UConn-USA....

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