

## 2024, PhD Position in condensed matter physics: Ferroelectric hybrid-Perovskites based semiconductors for optoelectronics: from synthesis to the investigation of physical properties

### Context:

Organic-inorganic hybrid perovskites have recently emerged as a new class of semiconductors resulting from the self-assembly of an inorganic structural framework within which organic cations are embedded [1]. Depending on the choice of the organic cation, the structural architectures of hybrid perovskites can be tuned from 3D (formula  $AMX_3$ ) to 2D (formula  $A_2MX_4$ ), 1D or 0D [Fig 1]. The resulting optical and electronic properties are strongly correlated to the connectivity of the semiconducting inorganic framework, the interaction between the organic and inorganic

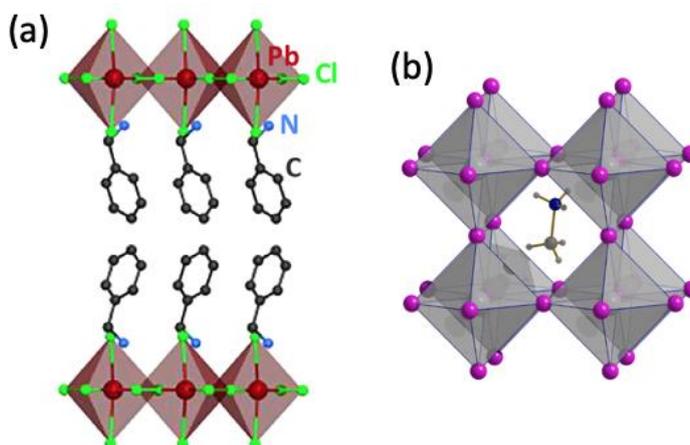


Figure 1: Structure of (a)  $(C_6H_5CH_2NH_3)_2[PbCl_4]$  and (b)  $(CH_3NH_3)PbI_3$ .

components, and the induced structural distortions. Chemistry is then an important tool to modify in a rational way the structure of hybrid perovskites and hence their physical properties. These materials exhibit applications in photovoltaics, optoelectronics (photo- or electroluminescent diodes, laser microcavities) and photodetection. In all of these, the perovskite is exposed to light excitation and electric field as a bias.

Electric field as an external perturbation could be an elegant and efficient way of controlling the structural distortions of perovskites [2]. Compounds without inversion symmetry present electromechanical properties (piezoelectricity and electrostriction), i.e. significant structural deformation induced by the application of an external electric field. These deformations strongly modify the electronic structure (in particular the value of the semiconductor gap) and the photoluminescence properties. Going further, the non-centrosymmetry coupled to a unique polar axis, leads to the apparition of a ferroelectric behaviour, i.e. the property of the material of having a spontaneous electrical polarisation that can be reversed by an external field [3]. Ferroelectricity is thought to be

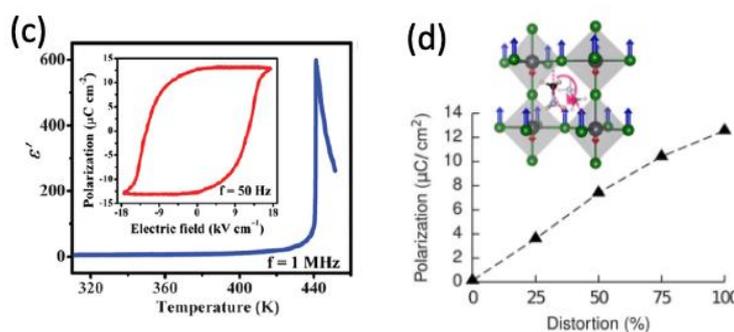


Figure 2: (c) P-E hysteresis loop and dielectric response of  $(C_6H_5CH_2NH_3)_2[PbCl_4]$ , (d) Simulation of polarisation VS the structural distortion in  $(CH_3NH_3)PbI_3$ .

responsible for excellent photovoltaic yields, by promoting the separation of charge carriers (electrons and holes) and their diffusion in solar cell geometry. First polarisation-voltage (P-E) cycles have been determined by piezo-force microscopy on 3D and 2D hybrid perovskite thin films, demonstrating ferroelectric properties fully competitive with the best inorganic ferroelectrics ( $BaTiO_3$ ,  $PbTiO_3$ ,  $PbZr_{1-x}Ti_xO_3$ ) [Fig 2]. In this context, we already studied the ferroelectric compound  $(C_6H_{11}NH_3)_2[PbBr_4]$ , which also exhibits remarkable photoluminescence [4]. Exploiting the piezoelectric and/or ferroelectric behaviour offers huge perspectives to develop new optoelectronic devices that can be driven by an external electric field: control of the gap or the efficiency and wavelength of photoluminescence, for example [5]. However, the ferroelectric properties of polar hybrid perovskites and their role in optoelectronic and photovoltaic mechanisms are still debated in the

literature, and poorly understood. In this PhD project, we propose to explore the structure-properties relationships of ferroelectric hybrid perovskites under electric field in order to provide a microscopic and structural description for the ferroelectric mechanisms and their influence on the physical properties.

### **PhD project:**

We will focus on two families of ferroelectric hybrid perovskites, 3D and 2D, derived from different organic cations, on which we will investigate the effects of the electric field as an external physical perturbation. The candidate will work on: i) Synthesis and growth of excellent large single-crystals of ferroelectric hybrid perovskites, ii) characterization of physical properties with optical absorption and photoluminescence spectroscopies under electric field ([CRM2](#)) and measurements of dielectric and ferroelectric properties (CAREL [Platform](#)) and iii) investigation of the structural features by X-ray diffraction under electric field.

### **Applicant:**

Candidates must hold a master's degree or an equivalent one (e.g. a diploma of an engineering school) with a solid training in solid-state physics or materials science. Knowledge in X-ray diffraction experiments will be an asset. The project involves close collaborations with experts in crystallography, electric and optical characterizations and condensed matter physics. The successful candidate is expected to have good ability for team work and dynamism on learning new skills. Applicants must be fluent in English and/or French with abilities in scientific writing.

### **Scientific environment:**

The project will take place at the Laboratoire de Cristallographie, Résonance Magnétique et Modélisations (CRM2), worldwide recognized laboratory for its expertise in advanced methods in crystallography and instrumental developments. The selected candidate will be hired in the "Crystallography and structure-properties relationships" team ([CRISP](#)). The candidate will find all the expertise and support needed to pursue her/his research work at CRM2 with CRISP's engineer in crystal growth and the engineers of the [PMD<sup>2</sup>X](#) platform. This project fits perfectly with the scope of the CNRS [HPERO GDR](#), in which the CRISP team contributes. This membership offers to the candidate opportunities of collaborations and contacts for the pursuit of her/his future career. This PhD project is funded by the University of Lorraine, with gross monthly salary about 2135 € and starting from 01/10/2024.

### **How to Apply:**

All application must be sent to the contact persons (hereafter), supported by a CV and a cover letter.

### **Contact (Supervisors) :**

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### **Related publications:**

- [1] B. Saparov, D. B. Mitzi, Chem. Rev. (2016), **116**, 7, 4558–4596; C. C. Stoumpos, M. Kanatzidis, Acc. Chem. Res. (2015), **48**, 2791–2802.
- [2] B. Chen, T. Li, Q. Dong, E. Mosconi, J. Song, Z. Chen, Y. Deng, Ye Liu, S. Ducharme, A. Gruverman, F. De Angelis, J. Huang, Nature Mater. (2018), **17**, 1020-1026.
- [3] S. Shahrokhi, W. Gao, Y. Wang, P. R. Anandan, M. Z. Rahaman, S. Singh, D. Wang, C. Cazorla, G. Yuan, J. M. Liu, T. Wu, Small Methods (2020), **4**, 2000149.
- [4] A. Yanguì, D. Garrot, J. S. Lauret, A. Lussion, G. Bouchez, E. Deleporte, S. Pillet, E. E. Bendeif, M. Castro, S. Triki, Y. Abid, K. Boukheddaden, J. Phys. Chem. C (2015), **119**, 23638–23647.
- [5] L. Ren, M. Wang, X. Guan, S. Wang, H. Yan, Z. Zhang, G. Yuan, T. Wu, Adv. Optical Mater. (2019), **7**, 1901092.