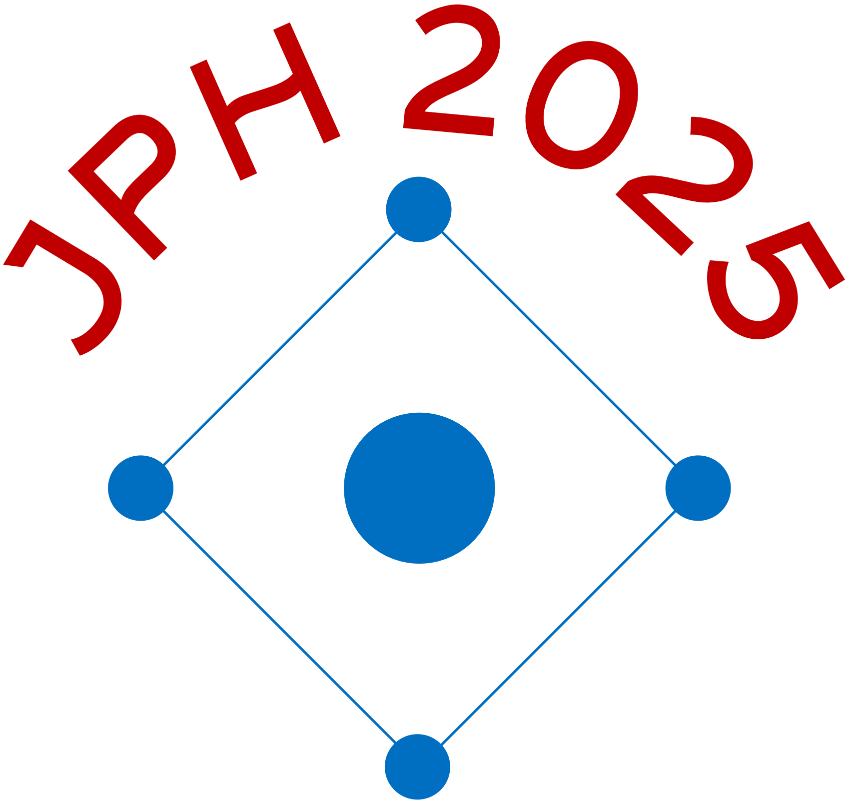

Journées Pérovskites Halogénées

Erquy, 19-21 mars 2025

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Tutorials

Perovskite Solar Cells : Operating Stability and Luminescence Imaging Characterisation

S. Cacovich[1]
[1] *IPVF, UMR 9006, CNRS, Palaiseau 91120, France*
E-mail: stefania.cacovich@cnrs.fr

Perovskite solar cells (PSCs) have emerged as a promising photovoltaic technology due to their high power conversion efficiency and low-cost fabrication. However, one of the critical challenges hindering their widespread commercialization is their limited long-term stability. PSCs are highly sensitive to environmental factors such as humidity, temperature fluctuations, and humidity exposure. These factors contribute to performance degradation over timescales ranging from hours to months, depending on synthesis conditions, encapsulation strategies, and operational stresses [1]. Understanding and addressing these stability issues is crucial for improving device reliability.

In response to these challenges, the solar cell research community has increasingly turned to optical imaging techniques, particularly luminescence-based methods, for materials and device characterization [2]. These techniques, which include photoluminescence (PL) and electroluminescence (EL) imaging, offer a non-destructive means of probing the fundamental optoelectronic properties of perovskite materials. They enable real-time assessment of key physical parameters such as energy gap and carrier recombination rates. Furthermore, photoluminescence imaging can be employed at multiple stages of a solar cell's lifecycle, from in-situ growth monitoring to operando performance evaluation under realistic working conditions. By using these advanced characterization tools, researchers can gain deeper insights into charge transport mechanisms and degradation processes, facilitating the development of more stable and efficient PSCs.

This tutorial will provide an overview of the stability challenges in perovskite solar cells and introduce the basic principles of luminescence imaging methods. Special emphasis will be placed on understanding recombination processes and degradation mechanisms, as well as optimizing imaging techniques for enhanced material and device analysis.

References

[1] Zhu, H., Teale, S., Lintangpradipto, M.N. et al. Long-term operating stability in perovskite photovoltaics. Nat Rev Mater 8, 569–586 (2023).
[2] Hameiri, Z., Mahboubi Soufiani, A., Juhl, M. K., Jiang, L., Huang, F., Cheng, Y.-B., Kampwerth, H., Weber, J. W., Green, M. A., and Trupke, T. (2015) Photoluminescence and electroluminescence imaging of perovskite solar cells. Prog. Photovolt: Res. Appl., 23: 1697–1705.

Materials design and atomistic modelling of perovskites for energy generation applications based on the density functional theory

G. Volonakis[1]
[1] Univ Rennes, CNRS, ENSCR, INSA Rennes, ISCR (Institute des Sciences Chimiques de Rennes)—UMR 6226, F-35000 Rennes, France
E-mail: yorgos.volonakis@univ-rennes.fr

Over the past decade, lead-halide perovskites have emerged as key materials for optoelectronic applications, including photovoltaics, sensors, and light-emitting diodes. In the first part of this tutorial, I will highlight recent advancements in developing alternative materials to traditional lead-halide perovskites. Computational design approaches based on first-principles calculations have played a crucial role in discovering new compounds, particularly within the halide double perovskite family. I will outline the computational strategies that guided the synthesis of these materials, emphasizing how first-principles insights facilitate synthesis, enhance optoelectronic properties, and enable the in-silico identification of compounds with characteristics akin to lead-halide perovskites. Additionally, I will present our latest findings on the electronic structures of various perovskite-based systems, including layered halide perovskites, vacancy-ordered double perovskites, and low-dimensional perovskite-like materials. For each class, I will discuss the key electronic features that dictate their optical properties and performance in experiments. These results shed light on the potential—both strengths and limitations—of these materials for diverse optoelectronic applications, from indoor and outdoor photovoltaics to light-emitting devices. Moreover, I will present our recent work on substitutional engineering in halide double salts, a promising class of materials for low-light photovoltaics, to showcase the power of density functional theory for materials modelling. Finally, if time permits, I will discuss state-of-the-art ab initio calculations of charge carrier transport in three-dimensional ABX_3 and layered halide perovskites. By directly examining the effects of structural dimensionality, our study reveals how carrier mobility is influenced by intrinsic carrier density in layered compounds, offering new insights into their transport properties.

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Invited contributions

Multicomponent Superlattices of Lead Halide Perovskite Nanocrystals

M. Bodnarchuk,[1,2] I. Cherniukh,[1,2] T. V. Sekh,[1,2] M. Svyrydenko,[1,2] C. Zhu,[2,1] E. Kobiyama,[3] G. Rainò,[2,1] T. Stöferle,[3] A. Travesset,[4] M.V. Kovalenko[2,1]
[1]Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland
[2] ETH Zürich, Switzerland
[3]IBM Zurich, Switzerland
[4] Iowa State University and Ames Lab, USA
E-mail: maryna.bodnarchuk@empa.ch

The past decade has seen the discovery and the rapid development of colloidal lead halide perovskite nanocrystals (LHP NCs) of $APbX_3$ stoichiometry. They offer unprecedented characteristics of their highly intrinsic excitonic photophysics: fast radiative rates and long excitonic coherence, as well as giant oscillator strength effects. LHP NCs are, therefore, attractivebuilding blocks for devising collective luminescence phenomena, such as superfluorescence, through self-assembly into superlattices. We reported a broad structural diversity in multicomponent, long-range ordered superlattices (SLs) comprising highly luminescent cubic $CsPbBr_3$ NCs (and $FAPbBr_3$ NCs) co-assembled with the spherical, truncated cuboid, and disk-shaped NC building blocks such as Fe_3O_4, PbS, $NaGdF_4$, and LaF_3 NCs [1,2]. These mesostructures also exhibit superfluorescence, characterized by high excitation density, by emission pulses with ultrafast radiative decay. The formation of such SLs was rationalized using entropy-maximization arguments and ligand-deformability. In the multicomponent LHP NC-only SLs comprising $CsPbBr_3$ NCs of different sizes as building blocks, efficient NC coupling and Förster-like energy transfer from strongly confined 5.3 nm $CsPbBr_3$ NCs to weakly confined 17.6 nm $CsPbBr_3$ NCs were observed [3]. The presentation will extend to the most recent work, wherein NCs are co-assembled with molecular entities or plasmonic NCs.

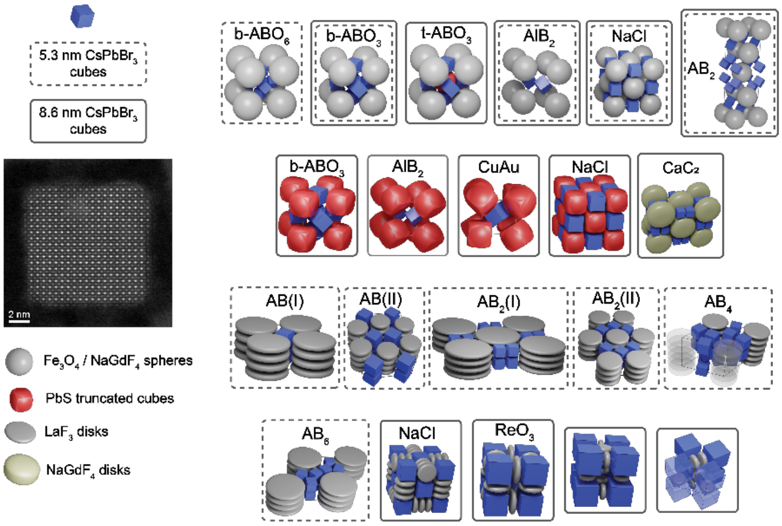

Figure | Diversity of binary superlattices obtained from $CsPbBr_3$ nanocubes combined with nanospheres, truncated nanocubes, and nanodisks

References

[1] I. Cherniukh, et al., *Nature*, **2021**, *593*, 535.
[2] I. Cherniukh, et al., *ACS Nano*, **2022**, *16,* 7210
[3] T. V. Sekh, et al., *ACS Nano*, **2024**, *18*, 11, 8423

In situ characterization techniques for understanding degradation in hybrid halide perovskites

F. Sauvage[1]

[1] *Laboratoire de Réactivité et Chimie des Solides, CNRS UMR7314, Université de Picardie Jules Verne, Hub de l'énergie, 15 Rue Baudelocque, 80039 Amiens Cedex, France*
E-mail: frederic.sauvage@u-picardie.fr

Hybrid halide perovskite has established its credibility as high performance thin film photovoltaic technology. In only one-decade, the hybrid organic-inorganic halide perovskite solar cell achieved to compete with all mature crystalline technologies, by reaching a certified 26.7% power conversion efficiency (PCE) on cells and 20.6% PCE on small modules [1]. Perovskite's strength stem from their remarkable opto-electronic properties. However, the technology still requires significant attentions regarding stability, in particular rapid structural and electronic degradation can be engendered when exposed to various external stressors (temperature [2,3], humidity [4-6], light [7,8], electrical bias [9]).

To cope with the long-term stability issue, it is a paramount to precisely understand the multiple degradation pathways of the perovskite upon and during the external stressing. To this end, *in situ* or operando characterization techniques are central tools. In this communication, we will be discussing the degradation of different perovskite composition on the basis of humidity or temperature-controlled *in situ* x-ray diffraction and corroborated with *in situ* electron spin resonance spectroscopy and *in situ* transmission electron microscopy. For example, one key finding which we will discuss is that α-$FAPbI_3$ degradation is substantially accelerated when temperature is combined to illumination and when it is interfaced with the extraction layers, and, second the existence of a temperature gap region which takes place only under illumination involving an intermediate stage between the thermal-induced perovskite degradation and the formation of PbI_2 by-product [10].

References

[1] NREL, PV research. Best Research Cell Efficiency Chart. https://www.nrel.gov/pv/cell-efficiency.html (accessed 2024-12-17).
[2] Ava, T. T.; Al Mamun, A.; Marsillac, S.; Namkoong, G. Applied Sciences 2019, 9 (1), 188.
[3] Ma, L.; Guo, D.; Li, M.; Wang, C.; Zhou, Z.; Zhao, X.; Zhang, F.; Ao, Z.; Nie, Z. Chem. Mater. 2019, 31 (20), 8515–8522.
[4] Lin, Z.; Zhang, Y.; Gao, M.; Steele, J. A.; Louisia, S.; Yu, S.; Quan, L. N.; Lin, C.-K.; Limmer, D. T.; Yang, P. Matter 2021, 4 (7), 2392–2402.
[5] Akman, E.; Shalan, A. E.; Sadegh, F.; Akin, S. ChemSusChem 2021, 14 (4), 1176–1183.
[6] Akhavan Kazemi, M. A.; Raval, P.; Cherednichekno, K.; Chotard, J.-N.; Krishna, A.; Demortiere, A.; Reddy, G. N. M.; Sauvage, F. Small Methods 2021, 5 (2), 2000834.
[7] Emelianov, N. A.; Ozerova, V. V.; Zhidkov, I. S.; Korchagin, D. V.; Shilov, G. V.; Litvinov, A. L.; Kurmaev, E. Z.; Frolova, L. A.; Aldoshin, S. M.; Troshin, P. A. J. Phys. Chem. Lett. 2022, 13 (12), 2744–2749.
[8] Akbulatov, A. F.; Luchkin, S. Yu.; Frolova, L. A.; Dremova, N. N.; Gerasimov, K. L.; Zhidkov, I. S.; Anokhin, D. V.; Kurmaev, E. Z.; Stevenson, K. J.; Troshin, P. A. J. Phys. Chem. Lett. 2017, 8 (6), 1211–1218.
[9] Anoop, K. M.; Khenkin, M.; Di Giacomo, F.; Galagan, Y.; Rahmany, S.; Etgar, L.; Katz, E.; Visoly-Fisher, I. Solar RRL 4 (1900335).
[10] Ruellou J., Courty M., Sauvage F., Adv. Funct. Mater. 2023, 2300811.

Lead Halide Perovskites for X-Ray Medical Imaging

E. Gros-Daillon[1]

[1]*CEA-Leti, Grenoble, France*
E-mail: eric.grosdaillon@cea.fr

In this talk, we will introduce the need for X-ray and gamma-ray detectors for medical imaging. This will include anatomical imaging by 2D radiography and 3D computed tomography as well as metabolic imaging by Single Photon Emission Computed tomography and Positron Emission Tomography. We will then review the state of the art in halide perovskite X-ray and gamma-ray detectors, based on scintillator and semiconductors, and we will trying to find out what this new class of materials can bring to detectors for medical imaging. Finally, we will focus on the development at CEA Grenoble of the next generation of medical flat panel detectors for medical radiography in integration mode based on halide perovskite semiconductors. [1-3]

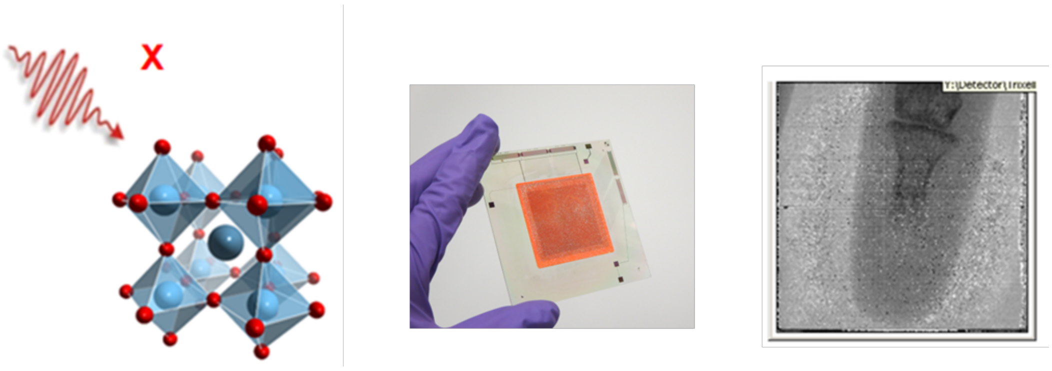

Figure | Prototype of a small X-ray imager based on metal halide perovskite and obtained radiographs.

References

[1] S. Amari, J. M. Verilhac, E. Gros D'Aillon, A. Ibanez, et J. Zaccaro, Cryst. Growth Des. **2020**, *20,* 3, 1665–1672

[2] O. Baussens, L. Maturana, S. Amari, J. Zaccaro, JM. Verilhac, L. Hirsch, E. Gros-Daillon, Appl. Phys. Lett. **2020**, *117*, 041904

[3] J.Ihrenberger, F. Roux, F. Lédée, F. Emieux, C. Anglade, T. Lemercier, G. Lorin, E. Gros-Daillon, and L. Grenet, Crystal Growth & Design **2024** *24 (13),* 5542-5548,

Chiral Halide Perovskite Materials for Optoelectronic and Spintronic Applications

A. Abhervé,[1] M. Maniadi,[1] K. Tieriekhov,[1] N. Mercier,[1] A. Kumar,[3] T. K. Das,[3] J. Even,[4] C. Katan,[4] M. Kepenekian[4]

[1] *MOLTECH-Anjou, UMR 6200, CNRS, UNIV Angers, France*
[2]*Department of Chemical and Biological Physics, Weizmann Institute of Science, Rehovot, Israel*
[3]*Univ Rennes, INSA Rennes, CNRS, Institut FOTON - UMR 6082, Rennes, France*
[4]*Univ Rennes, ENSCR, CNRS, ISCR – UMR 6226, Rennes, France*
E-mail: alexandre.abherve@univ-angers.fr

By combining the optoelectronic properties of halide perovskites (HPs) with chirality from inserted organic cations, chiral HPs brought new perspectives for chiroptical properties, such as circularly polarized luminescence (CPL), or spintronic devices such as spin valves or spin-LEDs, since chiral molecules can substitute ferromagnetic materials thanks to the chirality-induced spin selectivity (CISS) effect. We first revealed both experimentally (mc-AFM) and theoretically (band structure and spin texture calculations) the influence of crystal symmetry elements on the spin polarization ability of this family of materials [1]. More recently, we reported a full series of lead-free chiral double perovskites [2]. In combination with their lead-based counterparts, such series will ultimately allow us to investigate the fundamental role of metal ions on the CISS effect. On the other hand, revealing the chiroptical behavior of chiral HPs require a proper characterization of circular dichroism (CD) and CPL in the solid state, considering the macroscopic interferences inherent to highly crystalline thin films. An experimental guide to accurately discriminate between both intrinsic CD and macroscopic effects was recently reported with the example of 1D chiral lead-halides [3]. However, such effects can be minimized by controlling the orientation of the polar axis with respect to the light beam propagation, allowing artefact-free CPL characterization on both single crystals and thin films of 1D chiral lead-bromides with white-light emission (*manuscript under revision*).

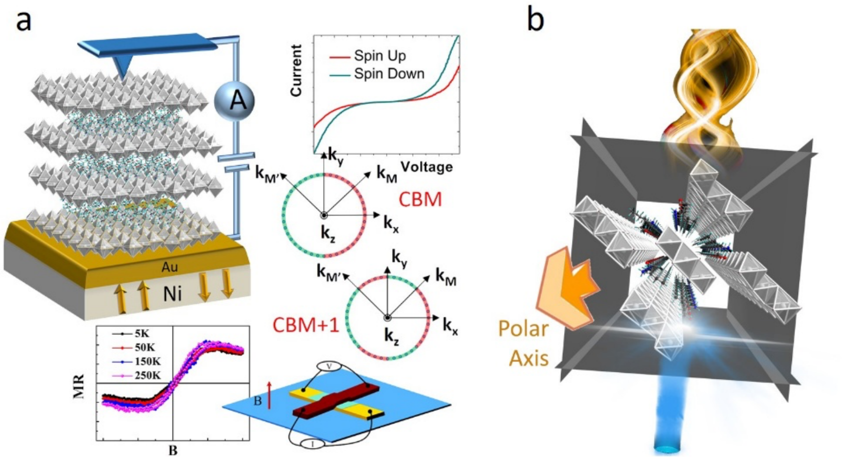

Figure | a) Spin polarization in a 2D lead-bromide perovskite. b) CPL in 1D lead-bromide network.

References

[1] A. Abhervé, N. Mercier, A. Kumar, T. K. Das, J. Even, C. Katan, M. Kepenekian, *Adv. Mater.* **2023**, *35*, 2305784.
[2] M. Maniadi, K. Tieriekhov, O. Ségut, N. Mercier, A. Abhervé, *Adv. Optical Mater.* **2024**, 2402949.
[3] A. Abhervé, *Adv. Optical Mater.* **2024**, *12*, 2400381.

Nanoscale Structural-Properties towards More Stable Perovskite Solar Cells

Zhuoying Chen

Laboratoire de Physique et d'Etude des Matériaux (LPEM), ESPCI Paris, PSL University, Sorbonne Université, CNRS UMR 8213, 10 Rue Vauquelin, F-75005 Paris, France
Email: zhuoying.chen@espci.fr

The achievement of both efficiency and stability in perovskite solar cells (PSCs) remains a challenging and actively researched topic. Under this context, our research team at LPEM strives to understand the degradation mechanisms and propose engineering methods to mitigate such effects. In this presentation, I will present two recent works to reveal the underlying physical and chemical processes involved in the passivation and degradation of functional PSCs.

On the aspect of engineering methods to fight against PSCs' instability, fluorinated molecules have shown good promise in the literature by enabling moisture barriers to some extent. Most of previous reported fluorinated molecules involve relatively short-chain molecules, enabling only a limited impact on the water-contact-angle of the perovskite surface. Here, our group investigated a series of fluorosilane molecules with different chain lengths aiming to achieve superhydrophobic perovskite surfaces. The decorated perovskite films exhibit strong tolerance to water thanks to a much larger water-contact-angle than those observed previously, reaching a maximum contact angle of ~130°. The optimized fluorosilane-decorated functional perovskite solar cells exhibit state-of-the-art power conversion efficiency (PCE > 22%) and prolonged storage lifetime under humid ambient environment than control samples without these molecules. In particular, by coupling nanoscale secondary ion mass spectrometry (NanoSIMS) mapping and infrared spectroscopy, I will discuss the underlying structural-property relationship of how these fluorosilane molecules decorate and passivate the perovskite active layer.

On the degradation of PSCs, I will present our recent work applying novel local electro-optical scanning technique to monitor the *in-situ* evolutions in terms of device interfacial temperature, photoluminescence (PL), and photovoltaic characteristics during device accelerated degradation. Here, the nano-scale probing of the device's interfacial temperature is made feasible by harvesting the upconversion fluorescence property of Er^{3+}-$NaYF_4$ colloidal nanoparticles which we synthesized in-house and inserted purposefully at the perovskite/HTL interfaces to serve as a nanothermometer. By combing the in-situ measurements and ex-situ structural and optical characterizations, I will discuss the different underlying physical and chemical processes happened during accelerated degradation and their complex interplay contributing to the overall observed properties of the degraded device.

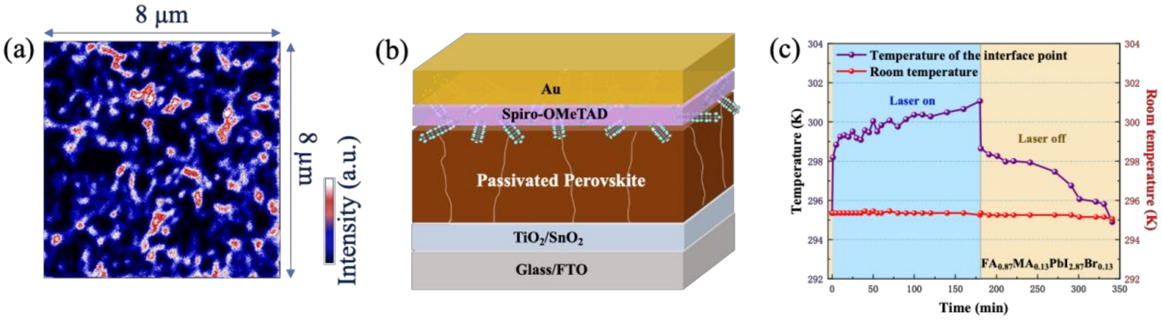

Figure caption: *(a) NanoSIMS mapping of the F-element from the top surface of a fluorosilane-passivated* $FA_{0.9}MA_{0.1}PbI_3$ *perovskite layer; (b) Schematic of the fluorosilane-passivated perovskite solar cell structure under investigation; (c) In-situ monitoring of the perovskite/HTL interfacial temperature during accelerated solar cell degradation triggered by the illumination of a blue laser (*λ *= 447 nm, 50 mW cm*$^{-2}$*) in ambient air.*

Polaritonic Metasurface Based on Halide Perovskite

Nguyen Ha My DANG[1], Trong Tam NGUYEN[1], Céline CHEVALIER[1], Gaëlle ALLARD[2], Emmanuel DROUARD[1], Emmanuelle DELEPORTE[2], Christian SEASSAL[1], Hai Son NGUYEN[1]
[1] *Ecole Centrale de Lyon, INSA Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, INL, UMR5270, Ecully 69130, France*
[2] *Lumière, Matière et Interfaces (LuMIn) Laboratory, Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupélec, 91190 Gif-sur-Yvette, France*
E-mail: hai-son.nguyen@ec-lyon.fr

Exciton-polaritons are half-light, half-matter excitations arising from the strong coupling regime between cavity photons and excitons of semiconductors. Behaving as superlative non-linear photons due to their hybrid nature, exciton-polaritons have been providing a fruitful ground for studying quantum fluid of light and realizing prospective all-optical devices.

In this presentation, we present experimental studies on exciton-polaritons in resonant metasurfaces, which are composed of sub-wavelength lattices of perovskite pillars (see Figure). Room temperature polaritons are demonstrated with a remarkable Rabi splitting in the 200 meV range. We show that polaritonic dispersion can be tailored on-demand. This includes creating linear, slow-light, and multi-valley shaped dispersions [1]. Moreover, we demonstrate that the strong coupling regime between perovskite excitons and photonic bound states in the continuum (BIC) leads to the formation of polariton-BIC that preserves the topological nature of its photonic component [2]. Finally, we observe experimentally the ballistic propagation of polaritons over hundreds of micrometers at room temperature, even with large excitonic components, some up to 75%. This long-range propagation is enabled by the high homogeneity of the metasurface, and by the large Rabi splitting which completely decouples polaritons from the phonon bath at the excitonic energy [3]. Our results suggest a new approach to study exciton-polaritons and pave the way for the development of large-scale and low-cost integrated polaritonic devices operating at room temperature.

$$|polariton\rangle = C|photon\rangle + X|exciton\rangle$$

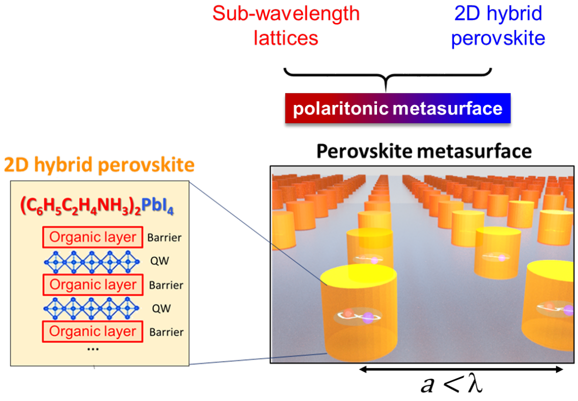

Figure | Illustration of polariton metasurface made of sub-wavelength lattices of perovskite pillars.

References

[1] Dang el al., Nano Letters 20 (3), 2113-2119(2020)
[2] Dang et al., Advanced Optical Materials 10, 2102386 (2022)
[3] Dang et al., Nano Letters, 38, 11839–11846 (2024)

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Journées Pérovskites Halogénées
Erquy, 19-21 mars 2025

Oral contributions

L’effet de l’introduction des monocouches auto-assemblées et l’orientation de la couche Transporteuse de trous sur les performances des cellules inverses à base de pérovskite hybride

Mohamed Ali ALOUI[1-2], Philippe LANG[1] , Radhouane CHTOUROU[2]
ITODYS[1] : Laboratoire Interfaces Traitements Organisation et DYnamique des Systèmes, Université Paris Cité.
LaNSER[2] : Laboratoire de Nanomatériaux et Systèmes pour Energies Renouvelables, Centre de recherche de technologie de l’energie (CRTEn)

Résumé : Ces dernières années, Les cellules à base de pérovskite hybride, sous ses différentes configurations ont connu une évolution spectaculaire due au mode de synthèse facile, à l’abondance des éléments chimiques formant ce matériau et notamment à son coût faible[1].Dans ce travail nous mettons l’accent sur l’effet de l’orientation de la couche sélective de trous(HTL) qui est l’oxyde de nickel (NiO) sous sa forme nanoparticule (isotrope) et celui qui est mieux orienté, synthétisé à base de précurseur Ni(acac)[2], faisant le lien entre l’état de l’oxyde de nickel et son influence sur les propriétés optiques et structurales de la couche active (MAPI) en ayant recours à différentes méthodes de caractérisation (DRX, UV-Visible et MEB).Ensuite, pour avoir un meilleur contrôle des interfaces on introduit les monocouches auto-assemblées dipolaire X-R-Y (SAMs) où (X= pole de greffage sur Mox ; R espaceur organique qui assure l’assemblage ;Y= pole terminal en interaction avec le film de Pérovskite hybride(PH))[3]. L’insertion de ces SAMs à pour objectif d’aligner les niveaux électroniques, de contrôler la croissance mono-orientée de la pérovskite hybride et de limiter les défauts de cristallisation [4].

Cette stratégie adoptée a permis l’amélioration de la stabilité ainsi que le rendement des cellules photovoltaïques.

Mots-clés : pérovskite, HTL, SAM.

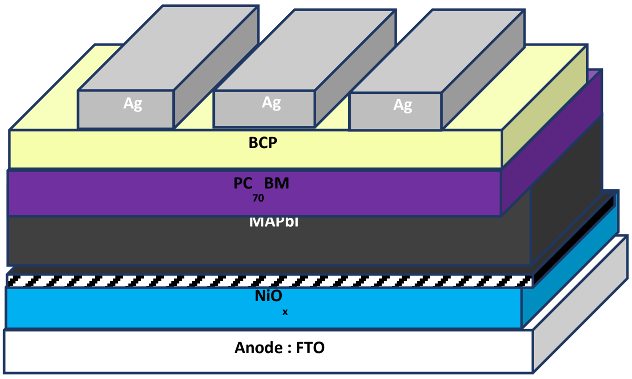

Figure 1 : Structure de la cellule inverse à base de pérovskite hybride

[1] Wang, R., Mujahid, M., Duan, Y., Wang, Z. K., Xue, J., & Yang, Y. (**2019**). A review of perovskites solar cell stability. *Advanced Functional Materials*, *29*(47), 1808843.
[2] Xu, L., Chen, X., Jin, J., Liu, W., Dong, B., Bai, X., ... & Reiss, P. (**2019**). Inverted perovskite solar cells employing doped NiO hole transport layers: A review. *Nano Energy*, *63*, 103860.
[3] F. Ali, C. Roldán-Carmona, M. Sohail, et M. K. Nazeeruddin, « Applications of Self-Assembled Monolayers for Perovskite Solar Cells Interface Engineering to Address Efficiency and Stability », *Adv. Energy Mater.*, vol. 10, no 48, p. 2002989, **2020**, doi: 10.1002/aenm.202002989.
[4] Youssef, M. B. (**2018**). *Fonctionnalisation de surface des oxydes métalliques par des SAMs dipolaires; application aux cellules photovoltaïques* (Doctoral dissertation, Université Sorbonne Paris Cité)

UP-SCALING PEROVSKITE GROWTH USING HYBRID METHODS FOR SILICON/PEROVSKITE TANDEM SOLAR CELLS

Kristell Carreric[1], Polyxeni Tsoulka[1], Louis Grenet[2], Elodie Gerente[2], Frédéric Roux[2], Solenn Berson[1]
[1] Univ. Grenoble Alpes, CEA, Liten, INES, 73375 Le Bourget du Lac, France
[2] Univ. Grenoble Alpes, CEA, Liten, DTNM, 38000 Grenoble, France
kristell.carreric@cea.fr

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In the last ten years, tandem solar cells based on perovskite (PK) materials have shown promising results, surpassing the theoretical limits of single junction Silicon (Si) solar cells. Even though Si/PK tandem solar cells appear capable of achieving 39,5% of power conversion efficiency [1], we need to overcome many challenges in order to upscale the PV devices and pass from the 1 cm² laboratory scale to larger areas. With that perspective, vapor deposition of the absorber layer seems promising in order to deposit a conformal and high quality perovskite on top of textured Si wafers. In the literature, the main industrially compatible techniques to grow the PK layer can be divided into two axes: i) PK deposition by full vapor deposition techniques and ii) PK deposition by hybrid processes (mix of a dry and wet process).

In this work, we focus on a hybrid deposition process where the first inorganic layer is grown by Close Space Sublimation (CSS). This technique allows high deposition rates (deposition time: a few minutes) [2], which would be more viable for the industry than other vapor deposition processes such as the thermal co-evaporation. The organic precursors are then deposited by spin coating in a second step, to convert the initial scaffold into the desired perovskite layer. Using different characterization techniques (X-ray Diffraction, X-Ray Photoelectron Spectroscopy, Scanning Electron Microscope, etc.) we firstly investigate the structural and chemical properties of the inorganic scaffold. The goal of this study is to understand how the homogeneity, the porosity and the composition of the first layer affect the growth of the final PK film. Simultaneously, we examine the key factors that influence the crystallization mechanism during the second wet step. Hence, we investigate the impact of parameters such as the ratio between organic precursors (*see* ***Figure 1***), the concentration of the organic solution, etc. Finally, we associate the material properties of the PK layer to the optoelectronic response of the PV devices (*see* ***Figure 2***). Our preliminary results on a full Si/PK tandem cell exhibited a record efficiency of 15,6%.

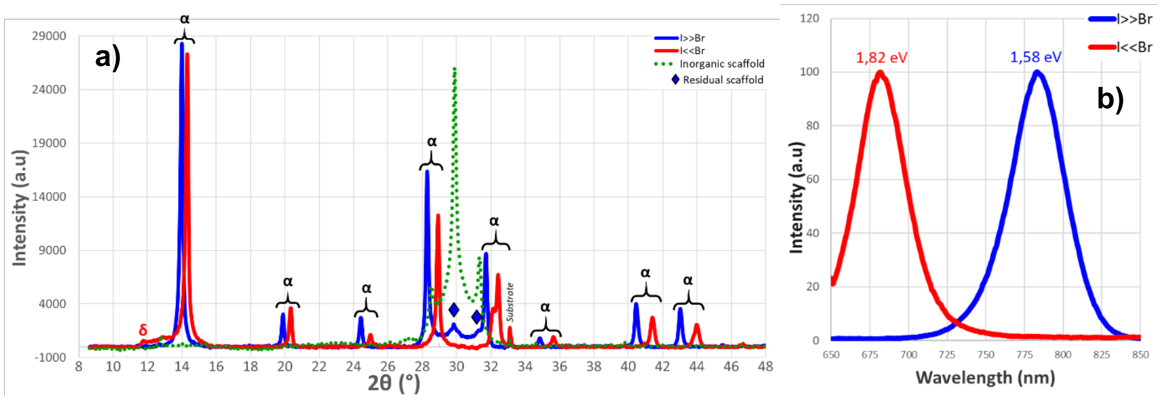

***Figure 1**: a) X-ray diffractogram of converted PK for two different ratios between halogens b) Photoluminescence spectra of the converted PK depending on the ratio between halogens*

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[1] O. Er-raji *et al.*, *Sol. RRL.* **2023**, 7, 2300659
[2] G. Zhang *et al.*, *ACS Appl. Energy Mater.* **2022**, *5*, 5797−5803

Mechanosynthesis of lead-free halide perovskites for supercapacitors

A. A. A. PIRZADO[1], V. DENAUD[1,2], T. KARAKOC[1], C. LEFEVRE[2], S. PRONKIN[1], S. BEGIN-COLIN[1*]

1 Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), UMR-7515, CNRS - Université de Strasbourg, Strasbourg 67087, France.

2 Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS - University of Strasbourg, 23, rue du Loess, 67034 Strasbourg Cedex 2, France.

**Corresponding author: Sylvie BEGIN-COLIN, Email : sylvie.begin@unistra.fr*

Halide perovskites have gained a lot of attention in energy storage applications due to their high electrical and ionic conductivity, large diffusion coefficients and ease of structural dimensions. However, some synthesis reproducibility issues and lead in the HPs composition could limit their commercial development [1]. In that context, we developed the mechanosynthesis (MS) of lead-free 2D and 3D perovskite powders for supercapacitor applications. Using this scalable and solvent-free synthesis technique, we have synthesized methylammonium copper bromide (MA_2CuBr_4), cesium bismuth chloride ($Cs_2Bi_3Cl_9$) perovskites, and MA_2CuBr_4-graphite composite powders, which are composed of aggregates of grains. The so-obtained powders were sieved at 50 and 150 micron size and then structural, optical and electronic characterizations were performed (X-ray diffraction, photoluminescence, and Raman spectroscopy) confirming the formation of the expected phase. Nevertheless, an additional washing step was necessary to obtain pure MA_2CuBr_4 powders and then only the orthorhombic crystal structure (with Pbca space group) was identified in XRD patterns [2].

MA_2CuBr_4 was first studied as an electrode material for supercapacitor and we have tested two electrolytes/working electrode systems. In the optimized LiPF6 electrolyte/Ti electrode system, MA_2CuBr_4 showed stable and high average specific capacitance of 205 Fards/gram (Fg^{-1}) for 20 cycles as a working electrode thanks to the 2D layered morphology suitable for lithium intercalation. The cyclovoltametric and charge/discharge experiments and comparisons with MS $Cs_3Bi_2Cl_9$, MA_2CuBr_4, and MA_2CuBr_4-graphite composite have evidenced the interest of such layered materials creating eco-friendly, high-efficiency lead-free hybrid perovskite devices for sustainable energy storage applications.

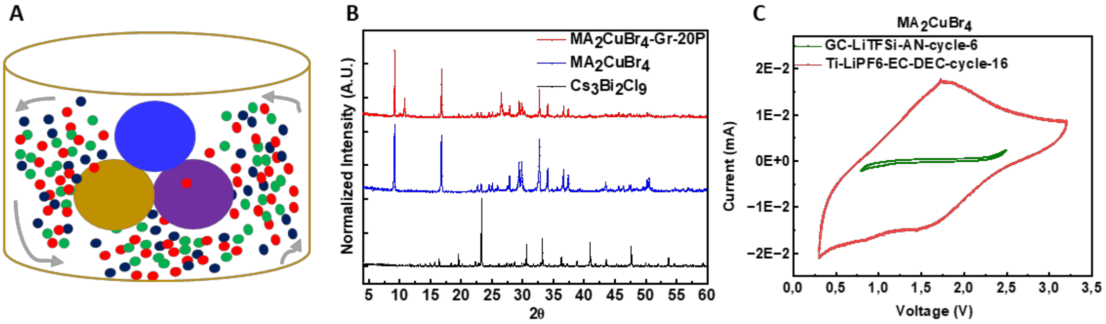


Figure | Graphical abstract of mechanosynthesis of lead-free perovskites for supercapacitors.

References

[1] A. Gaurav, A. Das, A. Paul, A. Jain, B. D. Boruah and M. Abdi-Jalebi, J. Energy Storage, 2024, 88, 111468
[2] P. Pandey, N. Sharma, R. A. Panchal, S. W. Gosavi and S. Ogale, ChemSusChem, 2019, 12, 3742–3746

From Mechanosynthesis to Photodetection: Exploring powder-based Low-Dimensional Hybrid Perovskite@Graphite Composites Wafer Devices

Yihui Cai[1], Azhar Ali Ayaz PIRZADO[1], Dominique Begin[1], Thomas Fix[3], Richard D. Schaller[4] Clément Sanchez[5,6], Sylvie Begin-Colin[1,2]

[1] ICPEES, UMR-7515 CNRS-Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, France.
[2] IPCMS, UMR-7504 CNRS-Université de Strasbourg, 23 rue du Lœss, 67034 Strasbourg Cedex 2, France.
[3] ICube, CNRS and Université de Strasbourg, 23 rue du Loess, BP 20 CR, 67037 Strasbourg Cedex 2, France.
[4] Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; Center for Nanoscale Materials, Argonne National Laboratory, Lemont, Illinois 60439, United States.
[5] Sorbonne Université, Collège de France, LCMCP, UMR 7574 CNRS, 4 place Jussieu, 75005 Paris, France.
[6] USIAS, 5 allée du Général Rouvillois, 67083 Strasbourg, France.
Corresponding author: sylvie.begin@unistra.fr

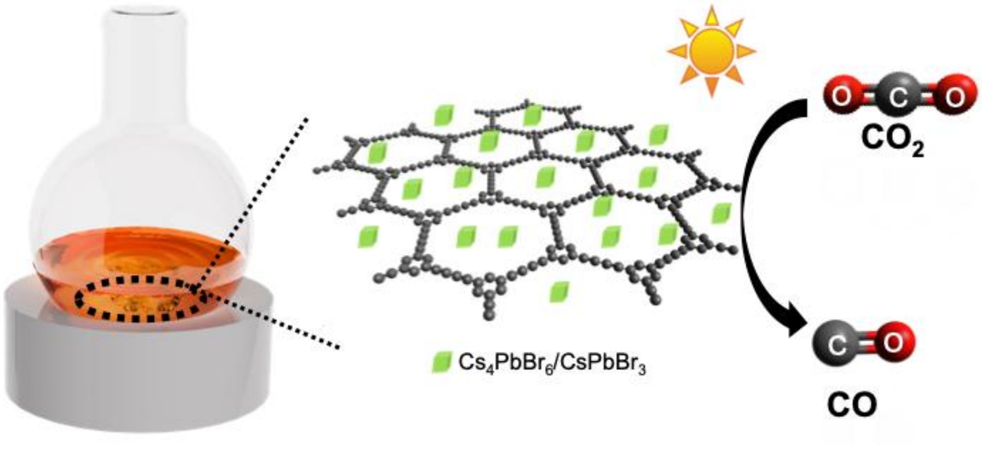
Besides 3D hybrid perovskites (HP), Ruddlesden-Popper (RP) phase low-dimensional HPs have gained huge research attention owing to their higher long-term stability and suppressed ion migration. In particular, the quasi-2D HPs display high photoresponsivity, good detectivity and fast switching time accompanied by better device stability. To enhance charge transfer, graphite or graphene can be used to improve conductivity and stability owing to their thermostability and hydrophobicity. Additionally, their layered structure affinity could favour interactions with RP HPs, enhancing device performance. For large-area photodetectors and industrial processing, large amounts and high-quality HPs are often required. Mechanosynthesis (MS) is a promising technique to produce quickly large quantities of high-quality powder as an eco-friendly alternative for HP synthesis.

In this work, we present the successful MS of low dimensional HPs: n= 1, 2, 3 HPs with three different organic ammonium cation spacers (*n*-butylammonium: BA; *n*-hexylammonium: HA and 2-phenylethylammonium: PEA) and their composites with 5 wt% graphite. To the best of our knowledge, it is the first time that the MS of the as-mentioned quasi-2D HPs and graphite composite was realized. These powders have been then compacted into wafers and photodetection measurements have been performed. The photoconducting behaviors evidenced an improved photoresponse in PEA^+-based HPs and composites by comparison with other HPs phases. The comparison of microstructural and optical properties of powder and wafers after compaction showed that compaction pressure impacted grain size, crystallite preferential orientation, and phase evolution in 2D HPs. However, above all, PL results reveal that compaction enables reduced reabsorption effects, allowing an enhanced surface emission, possibly attributed to the preferential grain orientation and lattice distortion. The compaction studies on n=2 BA^+- and PEA^+-based composites with 5 wt% graphite further confirm again the compaction-enhanced in-plane orientation and improved graphite integration with PEA^+ in quasi-2D HPs due to structural affinity and π- π interactions among aromatic rings and graphite. Therefore, the n=2 PEA^+-based wafer devices show improved charge transfer due to better-connected PbI_6 frameworks and π-π interactions, which are further enhanced by adding 5 wt% graphite. The PEA^+-based low dimensional HPs was shown to be a promising potential candidate for photodetection, especially its composite with graphite. This study offers a full picture into MS low-dimensional HPs and their graphite composites for photodetection, exploring the understanding of powder-compatible devices.

Hydrogen-substituted Graphdiyne combined with hybrid Perovskites toward photocatalytic CO_2 reduction

Thi Hieu Hoang,[1] Vien Duong Quach,[1] David Berardan,[2] Audrey Gayzal,[1] Joel Lemaire,[1] Mohamed Nawfal Ghazzal,*[1].
[1]Université Paris-Saclay, UMR 8000 CNRS, Institut de Chimie Physique, Orsay, 91405.
[2]Université Paris-Saclay, UMR 8000 CNRS, Institut de Chimie Moléculaire et des Matériaux d'Orsay, Orsay, 91405.
E-mail: mohamed-nawfal.ghazzal@universite-paris-saclay.fr

In response to the urgent need for sustainable and clean energy sources for the upcoming generations, converting CO_2 into fuel or chemical feedstock compounds could reduce, in principle, fossil fuel consumption and climate-changing CO_2 emission. One strategy aims to convert solar light to chemical fuel through the reduction of CO_2. In this context, photocatalysis involving light-irradiated catalysts offers both sustainable and relatively low-cost solutions to face the challenge. In this work, we investigate the CO_2 reduction under organic solution using H-substituted graphdiyne (HGDY) and perovskite composite. The perovskite was obtained by the dissolution-precipitation process, allowing the formation of the $Cs_4PbBr_6/CsPbBr_3$ junction in pyridine. Then, in situ growth of HGDY was performed under the presence of the perovskite, allowing solid composite formation. The material was characterized by TRPL, PL, TRMC, TPC, EIS, XRD, and TEM to shed light on the electronic and morphological properties. The results enable defining the charge transfer mechanism and the electronic properties of the composite, which was proven to be suitable for CO_2 reduction reactions. Indeed, our funding shows that H-GDY was revealed to play a crucial role in preventing the dissolution of perovskites in an aqueous solution, reducing photogenerated charge recombination, and improving charge separation efficiency. The hybrid HGDY/perovskite exhibits good activity and high selectivity to CO in CO_2 conversion.



Discovery of new hybrid alkali halide perovskite phosphors for LED applications

Shunfa.Gong,[1] Christopher.Hassam,[1] Romain Gautier[1]

[1]*IMN Institut des Materiaux de Nantes Jean Rouxel*
E-mail: Romain.Gautier@cnrs-imn.fr

Owing to the outstanding optoelectronical properties of hybrid lead halide perovskites, such as intense photoluminescence and adjustable band gap, this family of materials attracts a lot of attention. However, because of the lead toxicity, discovering new lead-free perovskite is urgent.

Through exploratory syntheses, we discovered new hybrid alkali halide perovskites $(PiPH_2)KI_3{\cdot}xH_2O$ (PiP=Piperazine, $C_4N_2H_{10}$), $(PiPH_2)RbI_3{\cdot}xH_2O$, $(PiPH_2)_3CsI_7{\cdot}xH_2O$. These materials prepared by simple synthesis methods from PiP, KI, RbI, CsI, and HI are non-toxic, based on abundant resources and exhibit a broad emission suitable for the fabrication of pc-WLED.

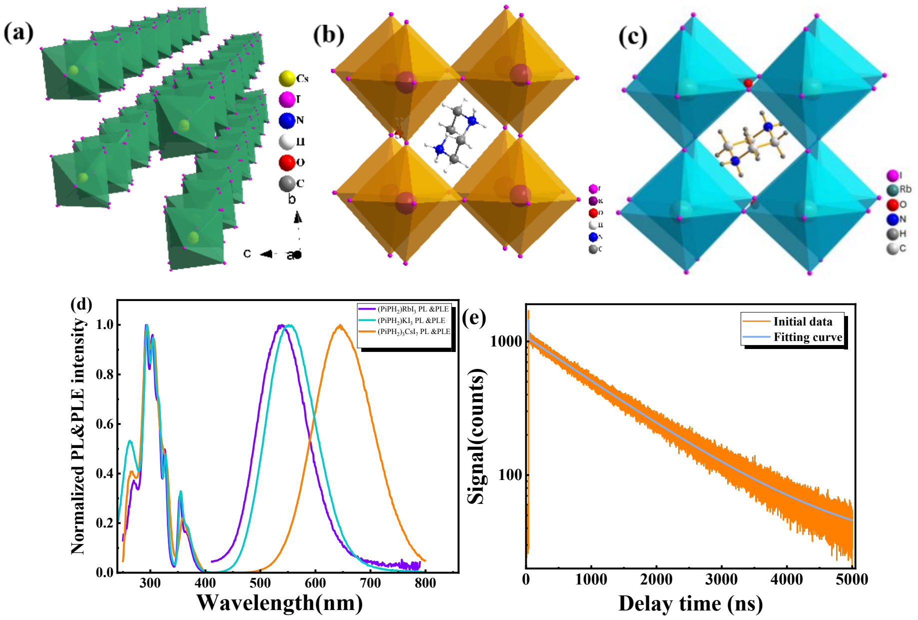


Figure (a-c) The crystal structures of $(PiPH_2)_3CsI_7{\cdot}xH_2O$, $(PiPH_2)KI_3{\cdot}xH_2O$ and $(PiPH_2)RbI_3{\cdot}xH_2O$ compounds. (d) The PL (Photoluminescence) and PLE (Photoluminescence excitation) spectra of alkali perovskites. (e) The time-resolved PL decays PL spectra of $(PiPH_2)_3CsI_7{\cdot}xH_2O$(Double exponential fitting).

Our work demonstrates for the first time that low-dimensional hybrid alkali halides exhibit photoluminescence properties. Thus, the one-dimensional structure $(PiPH_2)_3CsI_7{\cdot}xH_2O$ single crystals show red emission, with a maximum peak at 644 nm and a second harmonic generation response. Concerning the 3D perovskite structure, a $(PiPH_2)K_yRb_{1-y}I_3{\cdot}xH_2O$ solid-solution can be obtained by mixing KI and RbI in different ratios. The emission peak can be adjusted between 540-550nm by controlling the Rb/K element ratio. Other optical characteristics obtained by variable temperature fluorescence spectroscopy and time-resolved spectroscopy, revealed the luminescence originated from defects.

Distinguishing between photo-induced self-doping and valence transfer mechanisms in Gold-Based Double Perovskite.

Ange-B Chambissie Kameni[1], Alexandre Py-Renaudie[1], Javid Hajhemati[1], Damien Aureau[2], Matthieu Frégnaux[2], Davide Ceratti[4], Roberto Costantini[3], Martina Dell'Angela[3], Philip Schulz[1], Jean-François Guillemoles[1], Géraud Delport[1].

[1] CNRS, Ecole Polytechnique, Institut Photovoltaïque d'Ile-de-France UMR 9006, 91120 Palaiseau, France
[2] UMR 8180, CNRS, Institut Lavoisier de Versailles (ILV), Université de Versailles Saint-Quentin-en-Yvelines(UVSQ), 45 av. Des Etats-Unis, 78035 Versailles
[3] CNR-IOM, SS 14 – km 163.5, 34149 Basovizza, Trieste, Italy
[4]ParisTech-CNRS, PSL Research University, Institut de Recherche de Chimie Paris (IRCP), Paris , France
E-mail : ange-bernardin.chambissie-kameni@cnrs.fr

The observation of photoinduced ultrafast structural effects [1], such as phase transitions and valence transfer, are fascinating topics in solid-state physics. In this context, a recent study claimed the observation of photoinduced valence transfer [2-3] in gold-based double perovskites $Cs_2Au^{I}Au^{III}X_6$ (X = Cl, Br, I) [4], associated to the phototransmutation of Au^{1+}/Au^{3+} -> Au^{2+}. To investigate these effects, we employed a combination of time-resolved photoemission spectroscopy (TRPES, ALOISA Beamline, ELETTRA Synchrotron), coupled with laser excitation.

Rather than validating the photoinduced valence transfer, our results point toward a progressive self-doping and photodegradation. Finally, we obtained more information on such mechanism using complementary techniques such as time-dependent surface photovoltage (SPV) photoluminescence and self-healing measurements [5]. We collected evidence that such doping effect arises from halogen degassing in the thin films, eventually leading to the reduction of Au^{3+} -> Au^{1+} -> Au^{0} rather than Au^{1+}/Au^{3+} -> Au^{2+}.

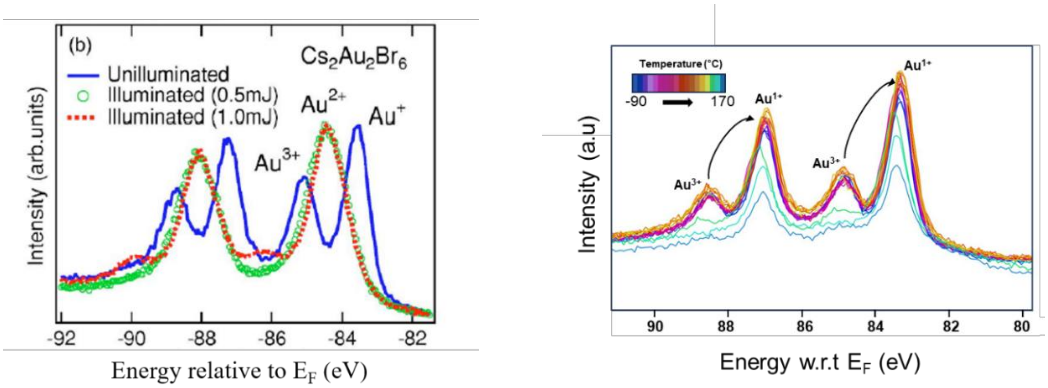


Figure | a) Au *4f* core level spectra under laser illumination at 300 K [2] b) Au *4f core level spectra* evolution with temperature under laser illumination in $Cs_2Au_2Br_6$ films.

References :

[1] Hervé M,Privault *et al*. Ultrafast and persistent photoinduced phase transition at room temperature monitored by streaming powder diffraction. Nat Commun **15**, 267 (**2024**).
[2] J-Y Son *et al.*, Phys.Rev.B. B, **2005**,72, p.1-4.
[3] Trigo,M *et al.* Ultrafast pump-probe measurements of short small-polaron lifetimes in the mixed-valence perovskite Cs2Au2I6 under high pressures. *Physical Review B—Condensed Matter and Materials Physics*, *85*(8), 081102.
[4] A.Py-Renaudie, Ange-B Chambissie Kameni et al., " Low-temperature synthesis of mixed valence gold halide perovskites and exploration of their photoluminescence properties", J.Mater.Chem.C,132646-2653 (**2025**).
[5] A. Py-Renaudie *et al.*, "Guided Search to Self-Healing in Semiconductors," *Adv. Funct. Mater.*, p. 2309107, **2023**.

Semi-Empirical DFTB Parameters for Bromide Perovskites: Electronic Structure Predictions in 3D, 2D, and Heterostructures

Junke Jiang,[1] Tammo van der Heide,[2] Simon Thébaud,[1] Carlos Raúl Lien-Medrano,[2] Arnaud Fihey,[3]
Laurent Pedesseau,[1] Claudio Quarti,[4] Marios Zacharias,[1] George Volonakis,[3] Mikael Kepenekian,[3]
Bálint Aradi,[2] Michael A. Sentef,[2] Jacky Even,[1] Claudine Katan[3]

[1]Univ Rennes, INSA Rennes, CNRS, Institut FOTON - UMR 6082, F-35000 Rennes, France
[2]Institute for Theoretical Physics and Bremen Center for Computational Materials Science, University of Bremen, 28359 Bremen, Germany
[3]Univ Rennes, ENSCR, CNRS, ISCR - UMR 6226, F-35000 Rennes, France
[4]Univ Laboratory for Chemistry of Novel Materials, Materials Research Institute, University of Mons, Place du Parc 20, Mons 7000, Belgium
E-mail: junke.jiang@insa-rennes.fr

Bromide-based perovskites have garnered considerable attention for their potential applications in optoelectronics and energy-related fields. However, reducing perovskite dimensionality from 3D to lower dimensions introduces challenges, especially with regard to quantum and dielectric confinement, which lead to larger band gaps and higher exciton-binding energies. Moreover, low-dimensional perovskite structures inherently require larger unit cells, making standard density functional theory (DFT) calculations computationally demanding. DFT can also significantly underestimate band gaps, posing additional obstacles in the accurate modeling of optoelectronic materials. Density Functional Tight-Binding (DFTB), a semi-empirical approach based on DFT, addresses these challenges by enabling simulations of large systems while offering reliable band gap predictions at reduced computational cost [1-2].

In this work, we present DFTB parameter sets specifically designed to accurately predict the electronic properties of bromide perovskites in both 3D (e.g., $CsPbBr_3$, $MAPbBr_3$, $FAPbBr_3$), and 2D forms (e.g., Cs_2PbI_4, BA_2PbI_4, PEA_2PbI_4, and BA_2PbBr_4). Benchmark comparisons with experimental measurements confirm the robustness of our approach in accurate band gaps and reduced effective masses prediction against experimental value. This first attempt is promising and can be applied to other low-dimensional (1D, 0D, hollow) perovskite nanostructures and more complex 2D/3D bromide perovskite heterostructures, which have demonstrated excellent operational stability in solar cell architectures.

References

[1] 1. B. Hourahine et al., *J. Chem. Phys.* **2020**, *152*, 124101.
[2] 2. J. Jiang, et al., **2024**, *arXiv preprint*, DOI: 10.48550/arXiv.2412.07016.

Vacancy type defects in hybrid lead halide perovskite and effect on positron capture and drift under voltage bias

P. Aversa[1], R. Helm[2], H. Jun[3], Y. Cai[4], J. Ihrenberger[5], H. Nahdi[1,6*], P. Desgardin[6*], D. Tondelier[3], J.E Bourée[3], S.Begin[4], F. Oswald[1], Y. Bonnassieux[3], J. Mitteneder[2], M.O. Liedke[7], K. Madaan[8,9*] G. Roma[9*], P. Pochet[8*], J. L. Liszkay[10], M.Butterling[8], M. Dickmann[2], A. Wagner[7], M.F. Barthe[6], W. Egger[2], B. Geffroy[1,3], C. Corbel[1]
[1] CEA/DRF/IRAMIS, University Paris-Saclay, Gif-sur-Yvette, France
[2] University of Bundeswehr, Munich, Germany
[3] LPICM, Institut Polytechnique de Paris, Palaiseau,
[4]ICPEES, Université de Strasbourg, Strasbourg, France
[5] CEA/LITEN/DTM, Grenoble Alpes University, Grenoble France
[6]CEMHTI, CNRS-Orléans, France
[7]HZDR, ELBE, Dresden, Germany,
[8] CEA/DRF/IriG, Univ. Grenoble-Alpes, France
[9] CEA/ DES/ISAS/DRMP/S2CM/SRMP, Université Paris-Saclay, France
[10] CEA/DRF/IRFU, Université Paris-Saclay, France
catherine.corbel@polytechnique.edu
**ANR Funding*

According to an extensive literature, halide-organic-inorganic lead perovskites (HOIPs) are considered to be mixed electronic-ionic conductors in which both carriers (electrons/holes) and ions can migrate under electric fields and/or ionising fluxes such as photons or X-rays. By providing a path for ion migration, crystallographic point defects can play a significant role in the degradation of the HOIP active layer and its interfaces in optoelectronic devices. In addition, for device performance based on the transport and collection of photocarriers at the layer interfaces, the question arises as to whether the carrier can be trapped at defects present near the interfaces.

The positron (e+) annihilation (PA) lifetime and the momentum distribution of e+-e- annihilating pairs reflect the electronic structure in which the annihilation takes place in matter. PA is used to characterise triple cation lead mixed halide, 3APbX, and/or methylammonium lead iodide, $CH_3NH_3PbI_3$, active layers in pin solar cells. Preparation and/or bias voltage are shown to affect the depth profile of the vacancy-type defects in the layer and the electronic structure at the electrode/ETL/HOIP interfaces.

The near-surface behaviour of the positron drift under bias voltage has characteristics that are completely different in 3APbX3 thin films than in n-type high quality silicon wafers. Positron drift is suppressed in 3APbX3 thin films near the electrode/ETL/3APbX3 interface. Possible reasons for the suppression of the positron drift are discussed. This feature is consistent with a high positron capture rate at vacancy-type defects, which significantly limits the drift distance.

Depending on the active layer preparation in the pin solar cell, three positron lifetimes, 366(1), 376(1) ps and ≥384 ps, are identified at room temperature as arising from different vacancy defect types with high concentration near the interface, which can hinder positron drift under electric field. These experimental lifetimes are compared with recent DFT calculations of positron annihilation lifetimes for the lattice or primary vacancy type defects in methylammonium lead iodide for the dominant tetragonal phase at room temperature. The DFT calculations vary with the treatment of the electron-positron correlation functional (EPCF). The comparison between experimental and calculated values can guide the choice of the appropriate EPCF treatment for defect identification.

Switchable second-harmonic generation and circular dichroism in chiral 2D double halide perovskites

M. Maniadi,[1] K. Tieriekhov,[1] O. Ségut,[1] D. Gindre,[1] E. Tailleur,[2] S. Pillet,[2] V. Dupray,[3] G. Volonakis,[4] N. Mercier,[1] A. Abhervé [1]

[1] MOLTECH-Anjou, UMR 6200, CNRS, UNIV Angers, 2 bd Lavoisier, 49045 ANGERS Cedex, France
[2] Universite de Lorraine - CRM2 - UMR UL-CNRS 7036, Boulevard des Aiguillettes Vandoeuvre, France
[3] SMS, UR 3233, Univ Rouen Normandie, Normandie Univ, F-76000 Rouen, France
[4] Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR - UMR 6226, France
E-mail: maria.maniadi@univ-angers.fr

In this context, we report new 2D double halide perovskite compounds, following the general chemical formula A(2 or 4)$Ag^{I}M^{III}Br_8$ where A is either the cystaminium dication ($Cyst^{2+}$) or the chiral cation (S/R)-1-(4-bromophenyl)ethylammonium (S/R-4BrMBA) and M^{III} = Sb^{3+}, Bi^{3+}. Cystaminium is known for its conformational axial chirality change in the solid state,[1] resulting in the synthesis of chiral perovskites which exhibit phase transition, leading to potential switchable SHG materials.[2] Driven by this objective, we synthesized and fully characterized the 2D $(Cyst)_2AgSbBr_8$ compound. Interestingly, four reversible phase transitions have been observed, with the SHG active Ph2 and the non SHG active Ph1 coexisting in a wide temperature range (5-42°C) rendering this compound ideal as a RT SHG switchable material (Figure a). The second spacer that we used was the chiral molecule S/R-4BrMBA, where a complete series of 2D bromide-based and iodide-based double perovskites was synthesized and fully characterized. Thin films were prepared in order to study the chiroptical properties of the materials. The thin films of $(S/R\text{-}4BrMBA)_4AgBiBr_8$ evolve from a single-phase compound with small circular dichroism signal to a polymorphic material showing a strong increase in the chiroptical response due to macroscopic effects, something which is not observed in the iodide derivatives (Figure b).[3]

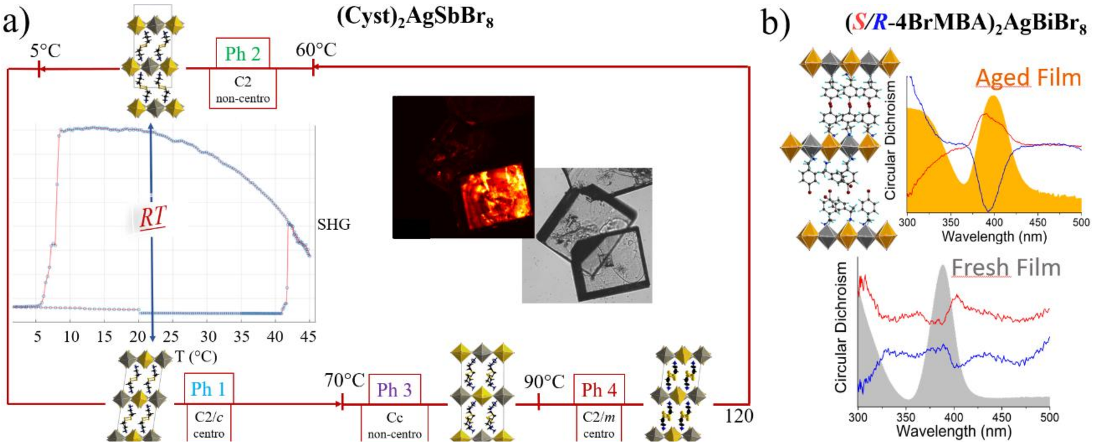


Figure | a) Schematic representation of the phase transitions and the SHG switch depending on the temperature, b) CD evolution based on the aging of the $(S/R\text{-}4BrMBA)_4AgBiBr_8$ films.

References

[1] N. Louvain, N. Mercier, J. Luc, B. Sahraoui, *Eur. J. Inorg. Chem.* **2008**, 3592-3596.
[2] N. Mercier, A. L. Barres, M. Giffard, I. Rau, F. Kajzar, B. Sahraoui, *Angew. Chem. Int. Ed.* **2006**, *45*, 2100-2103.
[3] M. Maniadi, K. Tieriekhov, O. Ségut, N. Mercier, A. Abhervé, *Adv. Optical Mater.* **2024**, 2402949.

Enhancing the Growth and Stability of Hybrid Perovskite Thin Films Using Self-Assembled Monolayers for Photovoltaic Applications

N. Balkis

The development of perovskite solar cells (PSCs) has seen remarkable advancements in recent years, with self-assembled monolayers (SAMs) playing a key role in improving device performance and stability. This work focuses on the use of SAMs, specifically CH2NH2-2PACz, to optimize the hole transport layer (HTL) in PSCs. We compare the impact of CH2NH2-2PACz with MeO2PACz, a widely studied SAM, on enhancing the HTL layer of NiO. Initially, CH2NH2-2PACz is introduced as a SAM to improve the quality of the NiO layer, enhancing charge transport and reducing recombination losses. In the second part of the study, CH2NH2-2PACz is explored as a direct HTL layer, replacing conventional materials to simplify the device structure and reduce fabrication costs. The effects of these SAMs and their modifications on the crystallization and stability of the perovskite layer, particularly under aging conditions, are systematically analyzedusing various characterization methods, including XPS, UPS ,XRD, UV-Vis spectroscopy, I(V)analysis.

This research highlights the potential of CH2NH2-2PACz as a promising SAM and HTL material for improving the efficiency and long-term stability of perovskite- based solar cells.

In-situ Multimodal Analysis of Metal Halide Perovskite Film Formation and Degradation for Stable Perovskite Solar Cells

Huriye Ertay[1], Davide Ceratti,[2] Tim Kodalle[3], Marion Provost[4], Carolin Sutter-Fella[3], Philip Schulz[1,4]
[1]*IPVF UMR, Palaiseau, France, 91120*
[2]ParisTech Chemistry - PSL University, Paris, France, 75005
[3]*Lawrence Berkeley National Laboratory, California, USA, 94720*
[4]Institut Photovoltaïque d'Ile-de-France (IPVF), Palaiseau, France, 91120
E-mail: huriye.ertay@cnrs.fr

Organic, inorganic lead halide perovskite solar cells have reached efficiencies comparable to silicon solar cells [1]. Despite achieving an impressive performance, perovskite solar cells still face significant challenges for outdoor implementation due to limited reliability and reproducibility where the interfaces between the halide perovskite absorber layer and adjacent charge transport films play a big part in the inherent stability of the cell component [2].

Here, we studied the effect of external stressors such as the exposure to air and humidity on triple cation ($Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(Br_{0.2}I_{0.8})_3$) perovskite on different substrates by using synchrotron-based in-situ Grazing Incidence Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) and photoluminescence (PL) spectroscopy measurements [3]. First, We carried out GIWAXS measurements whilst depositing perovskite on different substrates (e.g. SnO2 and NiO) to study perovskite crystallisation, where different crystallization kinetics can be observed for different charge transport layer deposition techniques. Furthermore, to advance our understanding of degradation, we carried out real-time GIWAXS and concomitant PL measurements as the perovskite degrades under different conditions where it was possible to detect different perovskite crystal structures, present heterogeneously, diminish with time as the PbI_2 concentration increased at the interface. We observed that different conditions triggered unique defect routes with different reaction kinetics.

References

[1] S. Liu, S. V. P. Biju, Y. Qi, W. Chen, Z. Liu, *NPG Asia Mater.* **2023**, *15*.
[2] P. Schulz, D. Cahen, A. Kahn, *Chem Rev.* **2019**, *119*, 3349-3417.

Optimizing Laser Scribing for High-Efficiency Perovskite Solar Modules with Minimal Dead Area

Andrés Soto,[1,2] Vera C. M. Duarte,[1,2] Adélio Mendes,[1,2] Luísa Andrade.[1,2]

[1]LEPABE – Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
E-mail: landrade@fe.up.pt

Perovskite solar cells (PSCs) have nearly reached the efficiency of traditional silicon-based cells, but face challenges in commercialization, such as long-term stability and large-scale manufacturing. A major issue is the loss of efficiency as the active area increases, primarily due to the increased series resistance of the transparent conductive oxide (TCO) electrode, which reduces the fill factor (FF) and, consequently, the device performance [1]. The P1-P2-P3 scribing process addresses this issue by connecting individual cells in series on the same substrate to form modules. Laser ablation is a preferred technique due to its precision and ability to produce smooth module structures [2]. In P1 ablation, the TCO layer is removed to create an insulating barrier; in P2 scribing, the hole transport layer (HTL), perovskite, and electron transport layer (ETL) are ablated to define sub-cells; and in P3 ablation, all layers except the TCO bottom electrode are removed for electrical isolation.

The optimization of the geometric fill factor (GFF), which defines the ratio between active and dead area, is crucial for maximizing the energy output [3]. In this study, the interconnection width (dead area) was minimized to achieve high GFFs in inverted perovskite solar modules with the structure: glass/FTO/PTAA/F-PEIA/$Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br_{0.15})_3$/F-PEIA/PCBM/BCP/Ag. A UV laser system (355 nm, 5 W) was used for ablation. The performance was evaluated by I-V curves , while the scribe morphology was analyzed by SEM and EDX. Using this approach, an interconnection width of 135 µm and a GFF of 99% were achieved.

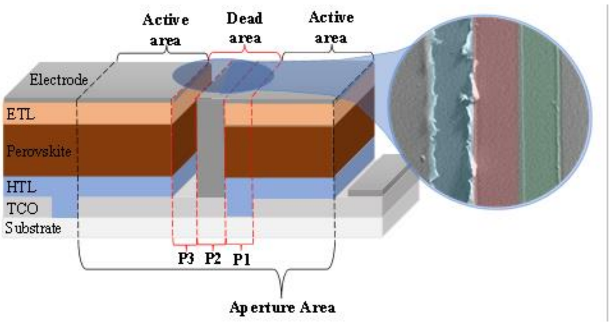


Figure | Schematic representation of an inverted PSC module, subdivided using the P1-P2-P3 method, and SEM image of the interconnection area, with P1 in green, P2 in red, and P3 in blue.

References

[1] Príncipe, J., et al., *Energy Technol.* **2022**, *10(4)*, 2100952.
[2] Jamaatisomarin, F., et al., *J. Manuf. Mater. Process.* **2023**, *7(3)*, 94.
[3] Di Giacomo, F., et al., *Micromachines.* **2020**, *11(12)*, 1127.

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This work was financially supported by project PTDC/EQU-EQU/4193/2021 with DOI 10.54499/PTDC/EQU-EQU/4193/2021 (https://doi.org/10.54499/PTDC/EQU-EQU/4193/2021) financed by national funds through the FCT/MCTES (PIDDAC); national funds through FCT/MCTES (PIDDAC): LEPABE, UIDB/00511/2020 (DOI: 10.54499/UIDB/00511/2020) and UIDP/00511/2020 (DOI: 10.54499/UIDP/00511/2020) and ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020).

Vibration intensity and Fröhlich electron phonon coupling in halide perovskite $CsPbBr_3$

Z. Xu[1], S. Thébaud[1], A. Létoublon[1], O. Durand[1], M. Zacharias[1], G. Volonakis[2], L. Pedesseau[1], M. Kepenekian[2], X. Zhang[3], D. Y. Chung[4], O. Bakr[3], M. Kanatzidis[4], S. Raymond[5], A. Ivanov[6], J. Ollivier[6], C. Katan[2], P. Bourges[7], J. Even[1]

[1]Univ Rennes, INSA Rennes, CNRS, Institut FOTON-UMR 6082, F-35000, Rennes, France
[2]Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, 35700 Rennes, France
[3]King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia
[4]Materials Science Division, Argonne National Laboratory, Lemont, IL 60439, USA
[5]Univ. Grenoble Alpes, CEA, INAC, MEM, 38000 Grenoble, France
[6]Institut Laue-Langevin, 38042 Grenoble, France
[7]Université Paris-Saclay, CNRS, CEA, Laboratoire Léon Brillouin, 91191, Gif-sur-Yvette, France
E-mail: Zeli.Xu@insa-rennes.fr

In recent years, 3D inorganic $CsPbX_3$ (X=Cl, Br, I) perovskite materials have gained popularity for their potential in various optoelectronic applications. These materials, especially as quantum dots, offer an attractive platform for classical and quantum light emission, exhibiting high photoluminescence quantum yield, broadband absorption, tunable emission wavelength and high photoluminescence stability[1,2,3]. For example, quantum lasers[4] and quantum computing[5] are considered to be their most promising applications.

However, the precise nature of the coupling between electrons and phonons in 3D $CsPbX_3$ perovskite materials remains unclear. This effect has potential to affect fundamental optoelectronic properties, including carrier mobility and excitonic effects. To access the electron phonon interaction, studying the lattice vibrations is the first step. We choose $CsPbBr_3$ as a typical material in our study due to its wide range of applications in quantum dots. To measure the lattice vibrations, we carry out coherent inelastic neutron scattering experiments. Well-defined optical phonon bundles are measured in $CsPbBr_3$. In order to further study the electron phonon coupling especially for optical phonons, we carry out first-principles calculations. Based on our simulation parameters, we calculate the electron phonon interaction strengths using the Fröhlich model as $CsPbBr_3$ is a strong polar semiconductor. In addition, the disordered structure is introduced to take into account the strong anharmonicity of this material[6]. The dominant optical mode of $CsPbBr_3$ is approximately 20 meV, which is consistent with temperature broadening of photoluminescence spectra and Raman scattering measurements reported for $CsPbBr_3$ quantum dots[7,8]. These results provide support for our ongoing theoretical studies on carrier-phonon interactions in disordered structures and excitonic polaron effects.

References

[1] C. Zhu et al., Advanced Materials, **2023**, 35(9): 2208354.
[2] Q. A. Akkerman et al., Science, **2022**, 377(6613): 1406-1412.
[3] P. Tamarat et al., Nature Communications, **2023**, 14(1): 229.
[4] Y. Park et al., Nature Reviews Materials, **2021**, 6(5): 382-401.
[5] A. J. Shields, Nature Photonics, **2007**, 1(4): 215-223.
[6] M. Zacharias et al. Phys. Rev. B, **2023**, 108, 035155.
[7] J. Ramade et al., Appl. Phys. Lett., **2018**, 12, 072104.
[8] C. M. Iaru et al., **2021**, Nature Communications 12, 5844.

Evidence of strong polar distortion and exciton polarons in lead-free mixed valence gold double perovskite.

Ange-B Chambissie Kameni[1], Alexandre Py-Renaudie[1], Damien Garrot[2], Baptiste Bérenguier[1], Philip Schulz[1], Jean-François Guillemoles[1], Géraud Delport[1]
[1]1 CNRS, Ecole Polytechnique, Institut Photovoltaïque d'Ile-de-France UMR 9006, 91120 PALAISEAU, France
2Université Paris-Saclay, UVSQ, CNRS, GEMaC, Versailles 78000, France
Corresponding speaker : geraud.delport@cnrs.fr

Double perovskites are emerging as promising alternatives to lead halide perovskites, addressing critical challenges such as toxicity and chemical instability. Among these materials, mixed-valence gold compounds[1]–[3] (e.g., $Cs_2Au^+Au^{3+}Cl_6$) have garnered significant interest due to their unique near-infrared absorption properties, making them highly attractive for optoelectronic applications. In this study, we employ optical spectroscopy to demonstrate that photoexcited species in these materials adopt a small polaronic nature, characterized by coupled electronic and phononic behavior. Thanks to combined characterization techniques (Raman and photoluminescence spectroscopy) we reveal the coexistence of two competing entities—charge polarons and exciton-polarons—whose equilibrium can be dynamically tuned by temperature variations or changes in optical excitation energy. These findings highlight the potential of mixed-valence gold double perovskites as a versatile platform for exploring and manipulating polaronic phenomena, paving the way for innovative advancements in next-generation optoelectronic devices.

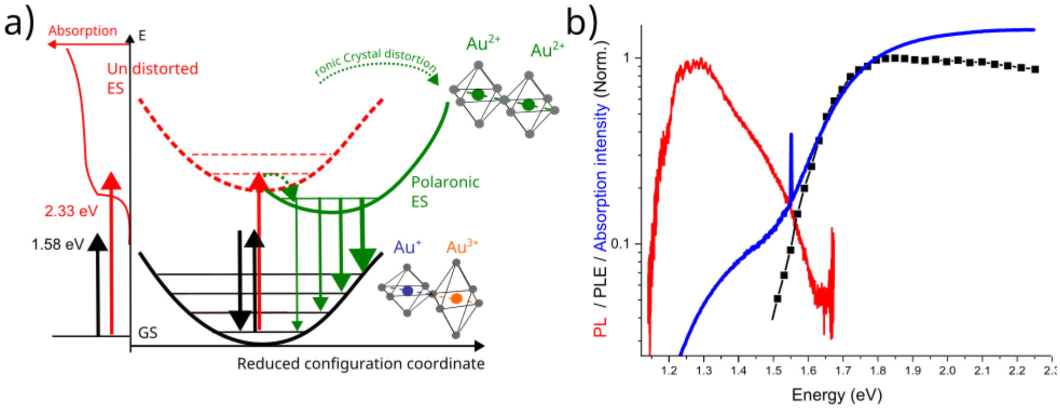

Figure1 : a) Energy diagram of the polar distortion , b) PL/PLE/Absorption spectra of $Cs_2Au^+Au^{3+}Cl_6$)

References:

[1] Alexandre Py, Ange B. Chambissie Kameni, Paul-Alexis Pavard, Nathanaelle Schneider, Géraud Delport, Pallavi Singh, Damien Aureau, Mathieu Frégnaux, David Cahen, Jean-François Guillemoles, "Low-temperature synthesis of mixed valence gold halide perovskites and exploration of their photoluminescence properties," *J. Mater. Chem. C*, vol. just accep, 2025.
[2] A. Py-Renaudie *et al.*, "Guided Search to Self-Healing in Semiconductors," *Adv. Funct. Mater.*, p. 2309107, 2023.
[3] S. Ramesh *et al.*, "Coherent Phonons, Localization and Slow Polaron Formation in Lead-free Gold Perovskite," *arXiv Prepr. arXiv2410.13401*, 2024.

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Posters

Electronic and Optical Properties of Sn/Ge Substituted 2D Dion-Jacobson Phase $(3\text{-AMPY})_4Pb_4I_{16}$ Perovskite for Photovoltaic Applications : A First Principle Study

F. G. Asefa [1,2], A. A. Arega[1], G. G. Kebede[1], C. Katan[2], M. Kepenekian[2], Y. S. Mekonnen [3]*, K. O. Obodo[4,5,6]

[1] Materials Science Program, CNCS, AAU, Addis Ababa, Ethiopia
[2] Univ Rennes, ENSCR, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), Rennes, France
[3] Center for Environnemental Science, CNCS, AAU, Addis Ababa, Ethiopia
[4] Center for space research, North-West University, South Africa
[5] ICTP-EAIFR, Kigali City, Rwanda
[6] National Institute of Theoretical and Computational Sciences, Johannesburg,South Africa
E-mail : frew.asefa@univ-rennes.fr

The structural, electronic, optical, and photovoltaic properties of Sn/Ge substituted 2D slightly shifted DJ phase $(3\text{-AMPY})_4Pb_4I_{16}$ perovskite were investigated using first principle calculations [1]. Pb atoms were substituted in the primary geometry by Ge and/or Sn and the structure as well as the stability of the new compositions were investigated. A total of nine configurations namely, $(3\text{-AMPY})_4Pb_4I_{16}$, $(3\text{-AMPY})_4Pb_{4-x}Ge_xI_{16}$, and $(3\text{-AMPY})_4Ge_{4-x}Sn_xI_{16}$ ($x = 1{-}4$) were examined. Their electronic band structures and partial densities of states reveal the well-known [2] dispersed valence and conduction bands build from metal s and halogen 5p orbitals with almost direct band gaps. The presence of molecular states close to the conduction band edge will be critically discussed. Real and imaginary dielectric functions were also computed and will be discussed in relation to carrier screening and optical absorption. To further assess their potential for photovoltaic applications, we computed their spectroscopic limited maximum efficiency based on the method proposed by Yu and Zunger [3].

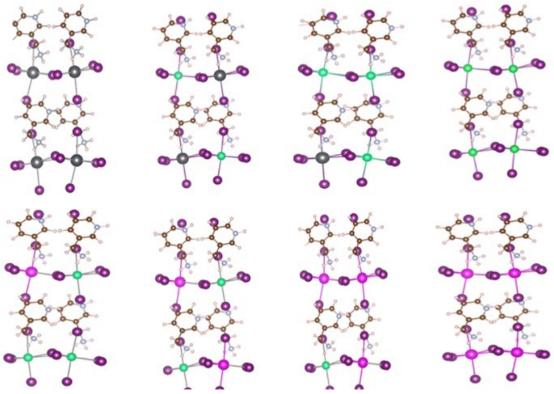

Figure | Optimized structures of $(3\text{-AMPY})_4Pb_{4-x}Ge_xI_{16}$, and $(3\text{-AMPY})_4Ge_{4-x}Sn_xI_{16}$ ($x = 0{-}4$).

References

[1] F. G. Asefa, A. A. Arega, G. G. Kebede , Y. S. Mekonnen, K. O. Obodo, J. Phys. Chem. C 2024, 128, 14158.
[2] J. Even, L. Pedesseau, M.-A. Dupertuis, J.-M. Jancu, C. Katan, Phys. Rev. B 2012, 86, 205301.
[3] L. Yu, A. Zunger, Phys. Rev. Lett. 2012, 108, 068701.

Synergistic Effects of Molecular Additives on Triple-Cation Mixed Halide Perovskite Photovoltaic Performance and Stability

Vishal Viswakarman[1,3], Miguel García Rocha[1,2], Johann Bouclé[3]

[1] Department of Nanoscience and Nanotechnology, Centre for Research and Advanced Studies of the National Polytechnic Institute (CINVESTAV-IPN), Mexico City, Mexico
[2] Department of Physics, Centre for Research and Advanced Studies of the National Polytechnic Institute (CINVESTAV-IPN), Mexico City, Mexico
[3]3Univ. Limoges, CNRS, XLIM, UMR 7252, F-87000 Limoges, France.

E-mail: johann.boucle@unilim.fr

Despite their notable power conversion efficiencies, formamidinium-cesium lead iodide ($FA_xCs_{1-x}PbI_3$) perovskite solar cells encounter ongoing stability challenges attributable to ion migration, phase segregation, and moisture sensitivity. In this study, a triple-cation mixed halide perovskite composition $(FA_xMA_{1-x})_yCs_{1-y}Pb(I_xBr_{1-x})_3$ is employed to enhance film homogeneity and structural stability. Building upon this optimized composition, a novel dual-additive engineering strategy is demonstrated, incorporating methylammonium chloride (MACl) and pyrrolidinium thiocyanate (PySCN) into the perovskite precursor solution. Through systematic materials characterization, it is established that this dual-additive approach significantly enhances the crystallographic properties and optoelectronic performance. X-ray diffraction analysis reveals improved crystal orientation, while scanning electron microscopy (SEM) and atomic force microscopy (AFM) confirm substantial grain size enhancement. Time-resolved and steady-state photoluminescence spectroscopy indicate superior defect passivation, evidenced by increase in emission intensity and extended carrier lifetime in films containing both additives. Notably, photovoltaic devices fabricated with the MACl-PySCN combination exhibit both enhanced power conversion efficiency and operational stability under standardized testing conditions. Current-voltage characterization reveals reduced hysteresis, while accelerated aging tests confirm improved device longevity. This study establishes that the combination of triple-cation mixed halide composition with strategic molecular additive engineering provides a viable pathway toward high-performance, stable perovskite photovoltaics. The demonstrated improvements in crystallinity, reduced hysteresis, and enhanced operational stability offer promising implications for advancing the commercial viability of perovskite solar technology. Our findings contribute valuable insights to the ongoing development of reliable and efficient perovskite photovoltaic systems, particularly in addressing the critical challenges of long-term operational stability and environmental resilience.

Excitation-Wavelength-Dependent Emission and White Emission of congruently melting Iodocuprate Hybrid Materials

Clémence CAZALS [1], Nicolas MERCIER [1], Romain GAUTIER [2], Florian MASSUYEAU [2], Mikaël KEPENEKIAN [3]

[1] MOLTECH-Anjou, University of Angers, Angers, France,

[2] IMN, Nantes University, Nantes, France

[3] University of Rennes, INSA Rennes, CNRS, ISCR, Rennes, France

E-mail: clemence.cazals@univ-angers.fr

In our work, we synthetized: 2D-(C4)CuI_2 **(1)** and 1D-(C3)CuI_2 **(2)** (Cn = $HO_2C(CH_2)_{n-1}NH_3^+$), which show excitation-dependent photoluminescence properties, an interesting class of materials [1]. Exciting at 380 nm, **(1)** and **(2)** exhibit red and pink emission (**(1)** τ = 18.9 ns), while in higher energy excitations (λ_{ex} = **(1)** 322 nm **(2)** 310 nm), they exhibit strong yellow and green emission, respectively (PLQY = 39 - 45%; **(1)** τ = 0.871 µs) (Fig.1). Low energy emissions (LE) may result from iodide vacancies (V_{I^-}) [2] activated from the organic part as revealed by DFT calculations (Fig.1a) while high energy emissions (HE), originate from cluster centered charge transfer (^{3}CC) (mix of halide to metal charge transfer (^{3}XMCT) and metal centered charge transfer (^{3}MC)) [3]. A nearly white phosphor converted LED (pc-LED) of **(1)** was obtained by using a LED sheet of 365 nm (Fig.1b). All compounds have a congruent melting, allowing solvent-free synthesis of the mixed metal compound (C4)$Cu_{0.5}Ag_{0.5}I_2$ exhibiting a nearly white emission (CIE: 0.39; 0.40 / CCT: 3799 K). Finally, by fast recrystallization, a metastable 1D phase of the **(1)** has been obtained exhibiting white emission (CIE: 0.32; 0.35 / CCT: 5949 K).

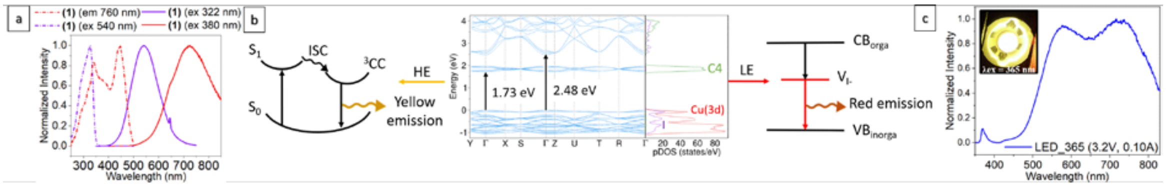

Figure | . PL and PLE spectra of **(1)** (a), Band structure and pDOS of **(1)** with emission mechanisms of HE (left) and LE (right) (b), Photography and spectra of pc-LED of **(1)** with a LED sheet of 365 nm (c).

References

[1] Dai, G.; Ma, Z.; Qiu, Y.; Li, Z.; Fu, X.; Jiang, H.; Ma, Z. J. Phys. Chem. Lett. **2022**, 13 (32), 7553– 7560
[2] Lin, G.; Zhao, F.; Zhao, Y.; Zhang, D.; Yang, L.; Xue, X.; Wang, X.; Qu, C.; Li, Q.; Zhang, L. Materials **2016**, 9, 990
[3] Ford, P. C.; Cariati, E.; Bourassa, J. Chem. Rev. **1999**, 99, 3625−3648

Mechanosynthesis of hybrid perovskite as an electromagnetic wave absorber

V.DENAUD[1,2], Y. Cai[1], C. LEFEVRE[2], S. BEGIN-COLIN[1*]

1 Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), UMR-7515, CNRS Université de Strasbourg, Strasbourg 67087, France.
2 Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS - University of Strasbourg, 23, rue du Loess, 67034 Strasbourg Cedex 2, FRANCE

*Corresponding author: Sylvie BEGIN-COLIN, Email: sylvie.begin@unistra.fr

The development of ever-increasing means of communication, such as 5G, and detection, such as military and civilian radars, is leading to an increase in the number of sources emitting electromagnetic waves and thus in strong electromagnetic pollution. This pollution can be the source of numerous interference problems between devices, as well as possible health problems. In that context, there is a strong need of new absorbent materials that are more effective and also over a wider frequency range. [1] Hybrid perovskites, and in particular MAPIs, are excellent dielectric materials with many polarisation modes that can be modulated according to frequency, making them excellent candidates for electromagnetic wave absorption (EMWA) application. [2] However, EMWA tests require large amount of powders to disperse within a polymeric matrix. Therefore, hybrid perovskites were elaborated by mechanosynthesis, a solvent-free method that enables producing large quantities of powders with good reproducibility and homogeneity. The grinding time has been shown to have an impact on the structural and optical properties of MAPI as well as on their defect level. Furthermore, MAPI ground for 4h was shown to display interesting EMWA properties by comparison with MAPI ground for 30 min. Therefore, we have studied the effect of grinding time of MAPI on their EMWA properties. Grinding times ranging from 30 minutes to 4 hours were chosen, and the resulting powders were then sieved and dispersed in a polymer matrix in order to measure their EMWA properties. The grain and crystallite sizes, the lattice parameters, the band gap, the static and transient photoluminescence, the surface properties by XPS have been determined. Then, the EMWA properties were correlated to these structural, optical and defect properties of MAPI as a function of grinding time. These results demonstrated that the mechanosynthesis allowed tuning the defect gradient in MAPI and enhancing the EMWA properties of MAPI.

References

[1] H. Lv, J. Cui, B. Li, M. Yuan, J. Liu, R. Che. *Adv. Funct. Mater.* 2024, 2315722

[2] Z. Zhang, Z. Xiong, Y. Yao, D. Wang, Z. Yang, P. Zhang, Q. Zhao, W. Zhou. *Adv. Funct. Mater.* 2022, 32, 2206053

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Modulation of magnetization in $BiFeO_3$ using circularly polarized light

Aseem Rajan Kshirsagar[1,2], **Sven Reichardt**[1]

[1]Department of Physics and Materials Science, University of Luxembourg, Luxembourg
[2*] Rennes Institute of Chemical Sciences (ISCR), University of Rennes, CNRS UMR 6226, France
*Current affiliation

$BiFeO_3$ is a multiferroic material featuring ferroelectricity and noncollinear antiferromagnetism. Definitive and efficient control of the characteristic spin texture of $BiFeO_3$ is attractive for emerging quantum devices. In this regard, crystal-field $d \rightarrow d$ excitations localized on Fe atomic sites in $BiFeO_3$ provide an avenue for manipulation of the spin texture as they induce a complex interplay among the spin, charge, and lattice degrees of freedom. In this work, the *ab initio* GW-BSE method is used to characterize these excitations within an excitonic picture. We find that the $d-d$ transitions appear as strongly bound, chiral, spin-flip excitons deep within the electronic band gap as a result of the intricate competition between the lattice potential, the antiferromagnetic ordering, the spin-orbit coupling, and the electron-hole interaction. Most crucially, these excitons are composed of electron-hole pairs with opposite spins that constitute almost all of their $\pm\hbar$ total angular momentum. These excitons of specific angular momentum can be selectively excited using circularly polarized light, consequently modulating the local magnetic moment.

[1] A. R. Kshirsagar, S. Reichardt, Phys. Rev. B **110**, 155131 (2024).
[2] A. R. Kshirsagar, S. Reichardt, arXiv:**2402.05430**, [cond-mat.mtrl-sci] (2024).

Introduction of Manganese atoms in 2D perovskite

Le Khanh Linh[1], Joël Cibert[1], Le Si Dang[1], Do Dinh Khai[2], Thuat Nguyen-Tran[2] and David Ferrand[1]
[1]Université Grenoble-Alpes, CNRS, Institut Néel, Grenoble, France
[2]VNU University of Science, Hanoi, Vietnam
E-mail: linh-khanh.le@neel.cnrs.fr; david.ferrand@neel.cnrs.fr

We report here the magneto-optical properties of Ruddlesden-Popper 2D perovskite $(PEA)_2PbI_4$ doped with manganese (Mn) atoms. Samples fabricated by cast-capping method are high quality single crystals with sizes up to 100 µm × 100 µm. We characterize the near band edge properties of Mn-doped samples by using micro-photoluminescence and micro-reflectivity measurements. We analyze the magnetic circular dichroism (MCD) in Faraday geometry with applied magnetic field up to 11T at different temperature. Our measurements show Zeeman splitting of a few meV corresponding to *g*-factor > 5, as well as a large change in the micro-photoluminescence intensity between the left and right circular polarizations in magnetic samples as reported in [1]. Furthermore, in reflectivity measurements, a sizable Zeeman shift with strong temperature dependence, and nonlinear in field, is observed. This result is attributed to the presence of manganese ions and its effect on the magnetic properties of host material. Our results show the potential for investigating the magnetic ions-carriers exchange interaction [1] as well as further studies of photo-induced ferromagnetism properties of 2D diluted magnetic perovskites [2].

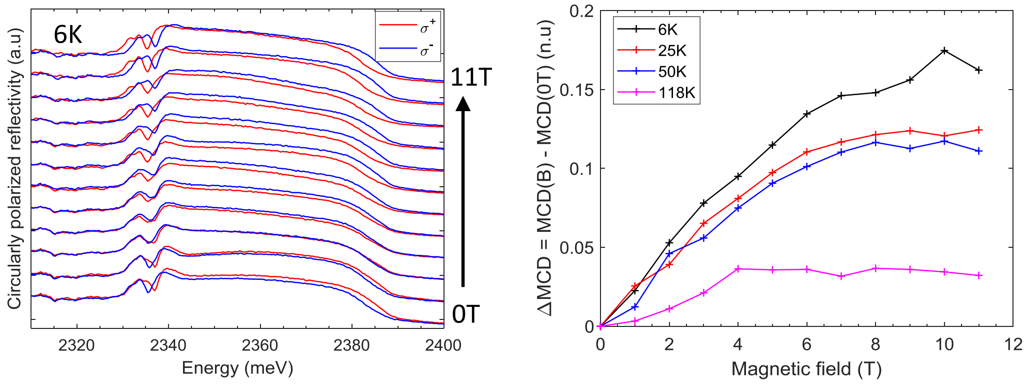

Figure | Magneto-reflectivity spectra at 6K (left) and reflectivity MCD spectra with temperature (right) of $Mn:(PEA)_2PbI_4$

References

[1] T. Neumann *et al.*, *Nat. Commun.* **2021**, *12*, 3489.
[2] S-H Lohmann et al., *Small.* **2021**, *17*, 2101527.

Single crystals and thin films of chiral hybrid perovskites for optoelectronics

S. Mathieu[1,2], A. Doudouh[1] E. Wenger[1], M. Zhu[2], M. Deutsch[1], S. Pillet[1], M. Stoffel[2]
[1]CRM2, CNRS, Université de Lorraine, Vandoeuvre-lès-Nancy, BP 70239, France
[2]Université de Lorraine, CNRS, Institut Jean Lamour, 54500 Nancy-France

E-mail: samuel.mathieu@univ-lorraine.fr

The introduction of large organic cations in the 3D hybrid halide perovskite (HHP) structure leads to perovskites of reduced dimension in which the inorganic octahedra organize themselves into either 2D planes or 1D wires with modified properties. Moreover, if the cation is chiral, it will transfer its chirality to the inorganic framework and the resulting chiral perovskite will exhibit chiroptic properties thanks to the chirality-induced spin selectivity effect (CISS). This opens the route to novel applications in the field of spin-optoelectonics such as the fabrication of spin light emitting diodes (spin-LEDs). In this work, we investigate the transfer of chirality in various single crystals such as (R/S-MBA)$_2$PbI$_4$ or (R/S-MBA)PbBr$_3$. Both structural characterizations as well as circularly polarized photoluminescence (CPPL) measurements are used to probe the chirality transfer. We further use thermal evaporation in a molecular beam epitaxy (MBE) chamber to obtain thin films of chiral HHPs , which could be building blocks of novel spin-LED devices.

References

[1] Brenner et al, *Nature Reviews Materials.* **2016**, *1*, 15007.

Operando spectroscopy imaging of the solar cell energy landscape

Chiara Mello[1], Poyoja Rout[2], Pilar Lopez Varo[3], Mathieu Frégnaux[4], Stefania Cacovich[1,3], Philip Schulz[1,3]

[1]Institut Photovoltaïque d'Île de France (IPVF), UMR 9006, CNRS, Ecole Polytechnique – IP Paris, Chimie Paristech – PSL, 18 boulevard Thomas Gobert, 91120 Palaiseau, France
[2]Centre for Nano Science and Engineering (CeNSE), Indian Institute of Science, 560012 Bengaluru, Karnataka, India
[3]Institut Photovoltaïque d'Ile-de-France (IPVF), 18 boulevard Thomas Gobert, 91220 Palaiseau, France
[4]UMR 8180, CNRS, Institut Lavoisier de Versailles (ILV), Université de Versailles Saint-Quentin-en-Yvelines (UVSQ), 45 avenue des Etats-Unis, 78035 Versailles, France

E-mail: chiara.mello@cnrs.fr

Metal halide perovskites (MHP) feature essential properties, such as high absorption coefficients, low exciton binding energy, long charge carrier diffusion lengths, and balanced charge transport, that make them ideal candidates for high-efficiency, low-cost photovoltaics. However, the interface between the perovskite active layer and charge transport layers (CTLs) plays a crucial role in determining both efficiency and stability. This work aims to develop a novel strategy to better understand and optimize these interfaces. To achieve this, we integrate X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) studies under operando conditions, allowing us to probe photochemical processes and their impact on the optoelectronic properties at the MHP/CTL interface. This approach enables us to correlate chemical insights, such as defect nature, stoichiometry, and oxidation states, with the energy landscape of the junction. Our investigation focuses on lateral heterojunction (LHJ) devices, which feature carrier-selective materials for back contacts and allow direct access to the active layer from the top [1, 2]. Specifically, we studied LHJ configurations using NiO_x and TiO_2 as selective contacts, interacting with double-cation $Cs_{0.3}FA_{0.7}Pb(Br_{0.1}I_{0.9})_3$ and triple-cation $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(Br_{0.17}I_{0.83})_3$ perovskites. We use these sample platforms to perform XPS measurements at synchrotron facilities under varying operating conditions, i.e. at varied bias voltage as well as in the dark and under illumination, to analyze core-level binding energies and variations of the chemical state of the perovskite film on top of the transport layers and across the channel between the two co-planar contacts [3]. In this way, we track transient processes in the perovskite such as ion migration and their impact on the electronic structure. While we find a bending of the core levels linked to ion migration, distinguishing this effect from secondary effects, such as electrical charging during the XPS experiment, remains challenging. To complement these findings, we perform PL mapping under open circuit conditions. We thus record microscopically resolved absolute PL spectra of the perovskite on top of the contacts and along the channel to assess bandgap variations and calculate the local quasi-Fermi level splitting (Δµ). We find that the bandgap remains stable across the sample, indicating no phase segregation. However, while double-cation perovskites appear more robust, achieving uniform, homogeneous thin films remains a challenge.

References

[1] Dunfield S.P., Bojar A., CRPS, **2021**, 2(8)
[2] Regaldo D, Bojar A. PIP, **2022**, 30(8), 994-1002

Exciton-Photon Strong Coupling in All-inorganic Perovskite Metasurface

Thi Anh Vui Nguyen[1], Trong Tam Nguyen[1], Emmanuelle Deleporte[3], Céline Chevalier[1],
Emmanuel Drouard[1], Christian Seassal [1,2], Hai Son Nguyen [1,2]

[1]Université Lyon, Ecole Centrale de Lyon, INSA Lyon, Université Claude Bernard Lyon 1,
CPE Lyon, CNRS, INL, UMR5270, Ecully 69130, France
[2] XLIM UMR CNRS 7252, Université de Limoges, Limoges, France
[3]Université Paris-Saclay, ENS Paris-Saclay, CentraleSupélec, CNRS, Lumière,
Matière et Interfaces (LuMIn) Laboratory, 91190 Gif-sur-Yvette, France
E-mail: vui.nguyen@ec-lyon.fr

Halide perovskites have been widely recognized as an excellent platform for exploring exciton-photon strong coupling regimes at room temperature. Among various approaches, subwavelength-scale perovskite metasurfaces offer precise engineering of light-matter interactions, enabling novel studies in this field. Recent advancements in hybrid organic-inorganic perovskite (HOP)-based metasurfaces have enabled exciton-polariton dispersion engineering [1], realization of polaritonic bound states in the continuum (BICs) [2], and long-range polariton propagation [3]. However, HOPs suffer from inherent stability limitations and have yet to demonstrate polariton lasing. On the other hand, most reports of polariton lasing have been observed in all-inorganic perovskites (AIPs), which offer enhanced chemical stability; but these studies have so far been limited to bulky microcavities. In this work, we fabricated $CsPbBr_3$ metasurfaces, using two methods: 1) Spincoating on a flat substrate followed by direct thermal nanoimprint at high pressure [4]; 2) Spin-coating on a pre-patterned substrate followed by recrystallization under high pressure (Figure 1a). As a result, the strong coupling regime is revealed in both angle-resolved reflectivity and photoluminescence measurements (Figure 1b), with Rabi splitting of approximately 180 meV. These findings highlight the potential of $CsPbBr_3$ metasurfaces for advanced photonic applications, paving the way for next-generation polariton-based devices. Moving forward, the next step involves exploring polariton lasing and condensation.

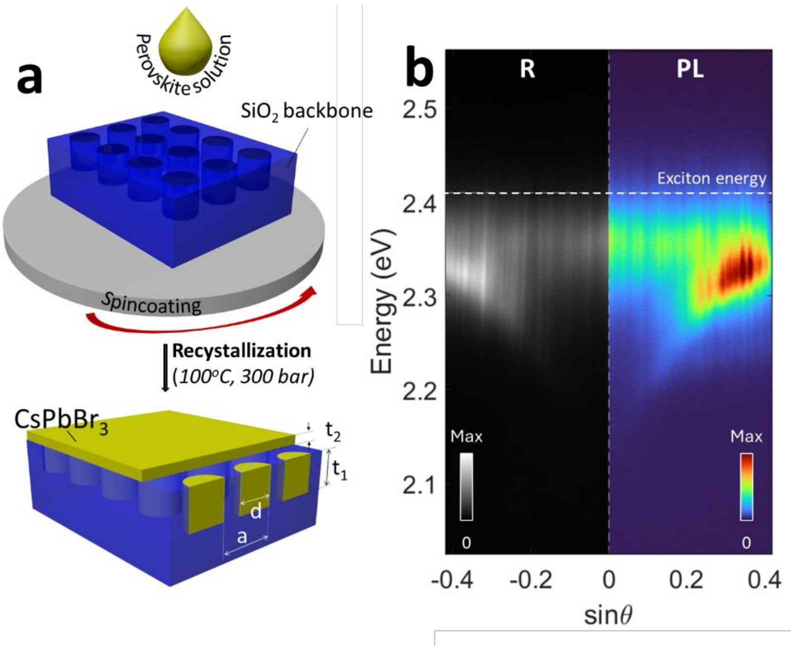

Figure 1|
(a) Sketch of metasurface structure fabrication.
(b) Angle- resolve reflectivity (right) and photoluminescence (left) of $CsPbBr_3$ metasurface.

References

[1] N. H. M. Dang et al. Nano Lett. **2020**, 20, 2113–2119.
[2] N. H. M. Dang et al. Adv. Opt. Mater. **2022**, 10, 2102386.
[3] N. H. M. Dang et al. Nano Lett. **2024**, 24, 11839-11846.
[4] N. H. M. Dang et al. Opt. Mater. Express. **2024**, 14, 1655-1669.

In-situ Investigations of the Thermal, Optical, and Photovoltaic Properties of Functional Perovskite Solar Cells during Degradation

Jiazhuo Nie, Dongjiu Zhang, Hengyang Xiang, Lionel Aigouy and Zhuoying Chen

Laboratoire de Physique et d'Etude des Matériaux (LPEM), CNRS UMR 8213, ESPCI Paris,
Sorbonne Université, Université PSL, 10 Rue Vauquelin, F-75005, Paris, France
Corresponding author: zhuoying.chen@espci.fr

Perovskite solar cells (PSCs) are considered to be one of the most promising emerging photovoltaic technologies due to their high power conversion efficiency (PCE) achievable by near-room-temperature solution-processing. In terms of PCE, this technology has witnessed a rapid growth from 3.8% [1] since early experiments in 2009 to over 26% nowadays [2]. Nevertheless, the material and device instability of PSCs remains a significant challenge, as they tend to degrade upon exposure to environmental factors, such as light, oxygen, humidity, and temperature [3]. The origins of such instabilities have been often linked to defect creation, phase segregation, ion migration, and decomposition. While it's relatively straightforward to evaluate the performance of solar cells ex-situ after degradation, in-situ measurements providing information simultaneously on the optical, electrical, and thermal property evolution of the devices are more complex to carry out but can provide valuable information to understand the degradation processes of PSCs.

In this work, we applied a novel local electro-optical scanning technique to monitor during device accelerated degradation the in-situ evolutions in terms of device interfacial temperature, photoluminescence (PL), and photovoltaic characteristics from functional PSCs based on two different compositions ($FA_{0.9}MA_{0.1}PbI_3$ and $FA_{0.87}MA_{0.13}PbI_{2.87}Br_{0.13}$). Here, the nano-scale probing of the device's interfacial temperature is made feasible by harvesting the upconversion fluorescence property of Er^{3+}-$NaYF_4$ colloidal nanoparticles which inserted purposefully at PSC interfaces to serve as a nanothermometer. By combing the in-situ measurements and ex-situ structural and optical characterizations, we discuss the different underlying physical and chemical processes happened during accelerated degradation and their complex contributions to the overall observed properties of the device.

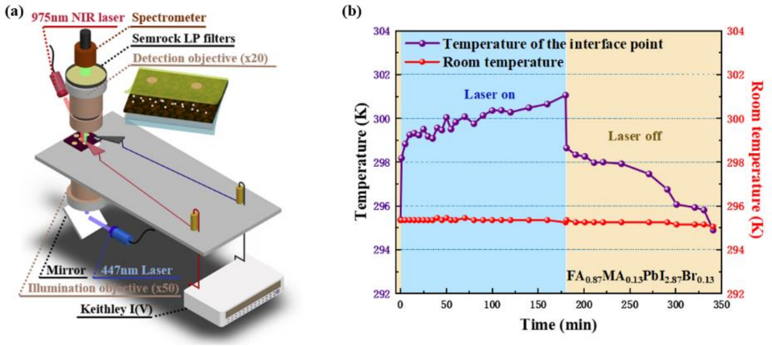

Figure | 1(a) Schematic diagram of experimental setup; (b) The observed temperature evolution of interface of the PSCs under blue laser degradation.

References

[1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, J Am Chem Soc 2009, 131, 6050.
[2] J. Zhou, L. Tan, Y. Liu, H. Li, X. Liu, M. Li, S. Wang, Y. Zhang, C. Jiang, R. Hua, W. Tress, S. Meloni, C. Yi, Joule 2024, 8, 1691.
[3] E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, M. D. McGehee, Chem Sci 2015, 6, 613

Rapid and Noise-Resilient Mapping of Photogenerated Carrier Lifetime in Halide Perovskite Thin Films

Tommaso Raimondi[1], Gabriele Scrivanti[1], Jean-François Guillemoles[1,2], Stefania Cacovich[1,2]

[1] Institut Photovoltaïque d'Île de France (IPVF), UMR 9006, CNRS, Ecole Polytechnique – IP Paris, Chimie Paristech – PSL, 18 boulevard Thomas Gobert, 91120 Palaiseau, France
[2] *Institut Photovoltaïque d'Ile-de-France (IPVF), 18 boulevard Thomas Gobert, 91220 Palaiseau, France*

E-mail: tommaso.raimondi@cnrs.fr

Photoluminescence imaging techniques are commonly used to measure the opto-electronic and transport properties of perovskite absorbers and devices [1], but achieving high precision requires longer acquisition times. Performing long experiments, due to the high reactivity of halide perovskites to external stimuli, can significantly alter these layers, compromising the quality of the data. We propose a method to extract high-quality lifetime images from quickly acquired, noisy time-resolved photoluminescence images [2]. This method effectively mitigates local signal-to-noise ratio (SNR) limitations, allowing access to greater detail and features in the results. Through simulations and experiments, we show that our method outperforms traditional pointwise techniques. Additionally, the analysis can be extended to determine the surface recombination rate. The determination of these key parameters can offer valuable insights into the advancement and optimization of halide perovskite materials. Indeed, the mitigation of bulk and interfacial recombination stands as a central focus within the solar cell community. Finally, we identify optimal acceleration and optimization parameters tailored for decay time imaging of perovskite materials, offering new insights for accelerated experiments crucial in degradation process characterization. Taking advantage of the reduced acquisition time, we tested this approach on halide perovskite thin films for in-situ humidity measurements, tracking the local evolution of carrier lifetimes. Importantly, this methodology has broader applications: it can be extended to other beam-sensitive materials various imaging characterization techniques, and more complex physical models for time-resolved decays.

References

[1] S. Cacovich, G. Vidon, **NC**, 13 (1), 1-9, 2022.
[2] G. Vidon, G. Scrivanti, **AFM**, 240234, 2024.

Charge transport properties, degradation phenomena and recombination mechanisms of perovskite materials, transport layers and interfaces

R. TAPADINHAS[1], W. FAVRE[2], O. BONINO[2], M. BOUTCHICH[2], J-P. KLEIDER[2]

[1]GeePs
[2]Centrale Supélec
[3]Sorbonne Université
[4]CEA INES
E-mail: raphael.tapadinhas@cea.fr

Perovskite solar cells (PSCs) are attracting increasing interest due to their high efficiency, both in single-junction and tandem configurations and for their low fabrication cost [1, 2].

However, the performance of PSCs can degrade over time, particularly under the influence of external factors such as light, humidity, and temperature [3]. This highlights the need for a deeper understanding of charge transport properties, recombination mechanisms, and degradation processes within the absorber and at the interfaces with charge transport layers (CTLs).

To address these challenges, test structures suitable for the electrical measurements of perovskite materials combined with CTLs will be developed. The design of these structures will need to consider the impact of the substrate type and successive depositions (CTL and metal) on the intrinsic properties of the perovskite. Several electrical / optical measurements will be investigated (Hall effect, conductivity, etc.) in order to improve our understanding of the carrier transport, both laterally and transversally, within the perovskite, the CTLs, and at their interfaces.

During the conference, the thesis objectives, test structures, characterisation methods, and initial results will be presented.

Thesis supervisors: Mohamed Boutchich, Wilfried Favre, Olivier Bonino, Jean-Paul Kleider
Thesis funding: PEPR TASE MINOTAURE

References

[1] S. Liu, V. P. Biju, Y. Qi, W. Chen, et Z. Liu, « Recent progress in the development of high-efficiency inverted perovskite solar cells », *NPG Asia Mater.*, vol. 15, n° 1, p. 1‑ 28, mai 2023, doi: 10.1038/s41427-023-00474-z.
[2] « Interactive Best Research-Cell Efficiency Chart ». Consulté le: 10 août 2024. [En ligne]. Disponible sur: https://www.nrel.gov/pv/interactive-cell-efficiency.html
[3] J. Zhou *et al.*, « Recent Advances in the Combined Elevated Temperature, Humidity, and Light Stability of Perovskite Solar Cells », *Sol. RRL*, vol. 6, n° 12, p. 2200772, 2022, doi: 10.1002/solr.202200772.

Impact of unintentional extrinsic and intrinsic doping on the electrical and nanostructural properties of $CsPbBr_3$

U. Teisson[1], C. Martin[2], F. Lédée[1], J.M. Verilhac[1], E. Gros-Daillon[2], J. Zaccaro[3]

[1]Grenoble Alpes University, CEA, LITEN, DTNM, F38000 Grenoble, France
[2]Grenoble Alpes University, CEA, LETI, DOPT, F38000 Grenoble, France
[3]Grenoble Alpes University, CNRS, Grenoble INP, Institut Néel, F38042 Grenoble, France
E-mail: ulysse.teisson@cea.fr

Halogenoplumbate perovskites exhibit interesting photoelectric properties, making them the subject of extensive study in many research areas such as photovoltaics, LED, photodetectors, etc… Their use as thick layers (>100µm) in direct X-ray detection devices could provide spatial resolution and sensitivity superior to that of indirect scintillator-based detectors [1]. This could for instance reduce exposure dose and pave the way for new medical applications (e.g. multi-energy radiography). To improve the performance and reproducibility of the devices, a deeper understanding of the physical and chemical properties of $CsPbBr_3$ dopants is required. Indeed, reducing doping levels could improve signal to noise ratio of the devices by lowering dark current. To this end, two PhD theses have been started at CEA Grenoble, aimed at studying the impact of unintentional extrinsic and intrinsic impurities on the electrical properties (e.g. charge transport) and nanostructural properties (e.g. defect density) of CsPbBr3.

One of the thesis started end 2024 aims at reducing the concentration of impurities. Unintentional dopants related to precursor purity and adsorption from the atmosphere will be studied through purification techniques such as recrystallization or sublimation [2][3] and by control of the working atmosphere. The analysis of impurities in $CsPbBr_3$ and its precursors will be carried on by ToF-SIMS, ICP-MS, ICP-OES, and XRD.

The second one started beginning 2025 aims at studying the impact of said impurities and their concentration on charge carrier’s properties (such as the nature, mobility and concentration of the carriers) using Hall Effect measurements [4]. In addition, defect spectroscopy techniques such as thermally stimulated current (TSC) will be carried on to determine the energy level and concentration of electrically active defects [5].

Combining the results will provide a better understanding of the impact of unintentional extrinsic and intrinsic impurities on $CsPbBr_3$ crystals doping, and ultimately, it will provide guidelines to reduce doping levels. The presented poster describes the methods and objectives of these works.

References

[1] C. C. Stoumpos, C. D. Malliakas, *Cryst. Growth Des.* **2013***, 13,* 2722–2727.
[2] D. Y. Chung, W. Lin, *Cryst. Growth Des*. **2024***, 24,* 9590–9600.
[3] R. A. Kerner, E. D. Christensen, *ACS Appl. Energy Mater*. **2023***, 6*, 295-301.
[4] A. Musiienko, D. Friedrich, *Nat Commun*. **2024**. *15*, 3016.
[5] Z. Lui, M.G. Kanatzidis, *J. Appl. Phys.* **2023***, 134*, 245101.

Light in-coupling in situ Transmission Electron Microscopy of inorganic perovskites for polaron analysis

F. Thorimbert,[1] E. Garnett[1,2]
[1]AMOLF Institute, Science Park 104, Amsterdam 1098XG, Netherlands
[2]Institute of Physics University of Amsterdam Science Park 904, Amsterdam 1098XH, Netherlands
E-mail: f.thorimbert@amolf.nl

Halide perovskites are at the center of numerous research and development efforts due to their optimal light harvesting properties, which can be tuned across the visible spectral range, particularly by mixing halides. However, mixed halide perovskites are unstable under illumination, as halide segregation leads to the formation of a two-bandgap region,[1] ultimately degrading solar cell performance. The underlying mechanism remains a subject of debate in the literature,[2] with one hypothesis suggesting that polarons play a role by inducing strain-driven phase separation at their formation sites. Polarons are photogenerated charge carriers accompanied by lattice distortions.

This talk focuses on investigating halide segregation to gain a better understanding of its mechanism through in situ illumination in an aberration-corrected TEM. We will report our observations of atomic-scale changes in pure bromide, $CsPbBr_3$, and mixed inorganic perovskites, $CsPb(I_xBr_{1-x})_3$ thin films and nanocubes under in-situ illumination with nanosecond time resolution. These effects include strain, halide phase separation and photoreduction to form lead clusters. We report on the effects of wavelength, intensity and photon dose on the photo-induced behavior. A particular emphasis is placed on the sample preparation to enhance the resolution of this nanoscale analysis. Finally, with this study, we aim to gain insights into the possible atomistic mechanisms underlying halide phase segregation.

References

[1]Hoke, E. T. *et al.* Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. *Chem. Sci.* **6**, 613–617 (**2015**).
[2]Brennan, M. C., Ruth, A., Kamat, P. V. & Kuno, M. Photoinduced Anion Segregation in Mixed Halide Perovskites. *Trends Chem.* **2**, 282–301 (**2020**).

Full series of (double) perovskite networks with (*S*/*R*)-3BrMBA or (*S*/*R*)-4BrMBA cations

Kostiantyn Tieriekhov, Alexandre Abhervé, Maria Maniadi, Nicolas Mercier, Olivier Ségut

MOLTECH Anjou, UMR-CNRS 6200, Univ Angers, 2 Bd Lavoisier, 49045 Angers, France
kostiantyn.tieriekhov@univ-angers.fr

Low-dimensional chiral perovskite networks play significant role in emerging field of chiro-spintronics. A variety of Pb-based compounds have been synthesized using commercially available chiral amines, among which (*S*/*R*)-methylbenzylammonium ((*S*/*R*)-MBA) [1] is of particular interest, since (S/R-MBA)$_2$PbX$_4$ have demonstrated potential for both optical applications and spin polarized current generation. Replacing Pb^{2+}, apart from practical necessity is vital to understand the role of metal ion in chiro-spintronic properties. So far, only four examples of chiral halide double perovskites (DP) using combinations of Ag^{+}Bi^{3+} and Ag^{+}Sb^{3+} have been described due to difficulties in crystallization of these compounds. This work describes the complete characterization of 2D Pb and AgBi bromide and iodide networks synthesized in our group based on 4BrMBA and 3BrMBA cations.[2] Thin film characterization techniques include XRD, GIWAXS and AFM, while advanced circular dichroism (CD) characterization approach allows to highlight the presence of macroscopic effects influencing the chiroptical response. The polymorphism occurring in thin films of both (4BrMBA)$_2$PbBr$_4$ and particularly (4BrMBA)$_4$AgBiBr$_8$ networks was confirmed by XRD data and strong evolution of CD performance. Intriguingly, the absence of the same evolution in thin films based on 3BrMBA demonstrates the role of chiral cation in fine-tuning the properties of the material – a valuable information for understanding the chirality-related phenomena in these series of compounds.

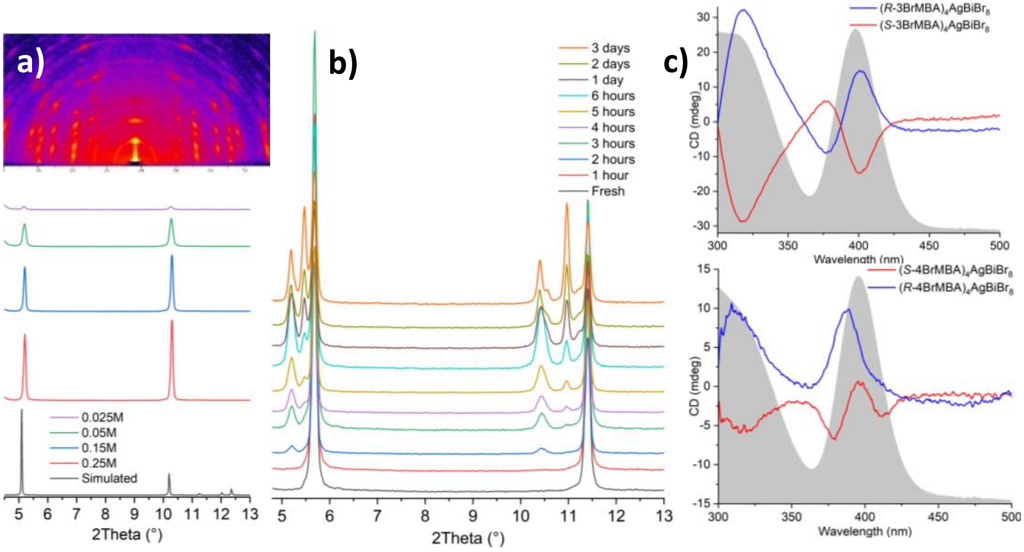

Figure |a) GIWAXS and XRPD characterization of (*S*-3BrMBA)$_4$AgBiBr$_8$; b) Time resolved XRPD study of (*S*-4BrMBA)$_4$AgBiBr$_8$ thin film; c) Absorption (grey area) and CD characterization of (*S*,*R*-4BrMBA)$_4$AgBiBr$_8$ and (*S*,*R*-3BrMBA)$_4$AgBiBr$_8$ networks.

References

[1] S. Ma, J. Ahn, J. Moon, *Adv. Mater.* **2021**, *33*, 2005760.
[2] M. Maniadi, K. Tieriekhov, O. Ségut, N. Mercier, A. Abhervé, *Adv. Optical Mater.* **2024**, 2402949

Synergistic Effects of Molecular Additives on Triple-Cation Mixed Halide Perovskite Photovoltaic Performance and Stability

Vishal Viswakarman,[1] Miguel García Rocha,[2] Johann Bouclé[3, *]

[1]*Department of Nanoscience and Nanotechnology, Centre for Research and Advanced Studies of the National Polytechnic Institute (CINVESTAV-IPN), Mexico City, Mexico*

[2]*Department of Physics, Centre for Research and Advanced Studies of the National Polytechnic Institute (CINVESTAV-IPN), Mexico City, Mexico*

[3]*Univ. Limoges, CNRS, XLIM, UMR 7252, F-87000 Limoges, France*

[*]*E-mail: johann.boucle@unilim.fr*

Despite their notable power conversion efficiencies, formamidinium-cesium lead iodide ($FA_xCs_{1-x}PbI_3$) perovskite solar cells encounter ongoing stability challenges attributable to ion migration, phase segregation, and moisture sensitivity. In this study, a triple-cation mixed halide perovskite composition $Cs_{1-y}(FA_xMA_{1-x})_yPb(I_xBr_{1-x})3$ is employed to enhance film homogeneity and structural stability. Building upon this optimized composition, a novel dual-additive engineering strategy is demonstrated, incorporating methylammonium chloride (MACl) and pyrrolidinium thiocyanate (PySCN) into the perovskite precursor solution. Through systematic materials characterization, it is established that this dual-additive approach significantly enhances the crystallographic and photophysical properties of the polycrystalline films. X-ray diffraction analysis (XRD) reveals improved crystal orientation, while scanning electron microscopy (SEM) and atomic force microscopy (AFM) confirm substantial grain size enhancement. Time-resolved and steady-state photoluminescence spectroscopy indicate better defect passivation, evidenced by increase in emission intensity and extended carrier lifetime in films containing both additives. Notably, photovoltaic devices fabricated with the MACl-PySCN combination exhibit both enhanced power conversion efficiency and operational stability under standardized testing conditions. Current-voltage characterization reveals reduced hysteresis, while accelerated aging tests confirm improved device longevity. Our findings contribute valuable insights to the ongoing development of reliable and efficient perovskite photovoltaic systems, particularly in addressing the critical challenges of long-term operational stability and environmental resilience.

Fluorosilane Facilitates Highly-Efficient and More Stable Perovskite Solar Cells

Dongjiu Zhang [1], Jiazhuo Nie [1], Smail Mostefaoui [2], Sergio Vlaic [1], Laurent Billot [1], Jérôme Aleon [2], Lionel Aigouy [1], and Zhuoying Chen [1]

1. *Laboratoire de Physique et d'Étude des matériaux (LPEM, CNRS-UMR 8213), ESPCI Paris, PSL University, 10 Rue Vauquelin, 75005 Paris, France*

2. *Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (CNRS UMR7590) Museum National d'Histoire Naturelle, CP 52, 57 rue Cuvier, 75231 Paris Cedex 05, France*

Corresponding author: zhuoying.chen@espci.fr

Abstract: Organic-inorganic hybrid perovskite solar cells (PSCs) have exhibited excellent photovoltaic performance comparable to conventional silicon solar cells, except for their non-negligible poor long-term stability induced by various environmental factors (e.g., moisture, oxygen, and ultraviolet (UV) light). Especially in the presence of moisture environments, PSC devices are particularly prone to degradation. To this regard, in the literature, different short-chain fluoromolecules have been experimented suggesting their promise. Nevertheless, most of these fluoromolecules previously experimented are short-chain molecules exhibiting limited effect on the water-contact-angle of the perovskite layer. In this work, we investigate the possibility to design superhydrophobic surface to enhance the stability of PSCs in humid environment. Three fluorosilanes with different chain lengths are utilized to modify the perovskite film through vapor-assisted self-assembled process. The decorated perovskite films exhibit outstanding tolerance to water thanks to a much larger water-contact-angle than those observed previously, reaching a maximum contact angle > 130°. The optimized fluorosilane-decorated functional perovskite solar cells exhibited state-of-the-art power conversion efficiency (PCE > 22%). More importantly, under identical degradation conditions, they exhibited only a 4% of PCE drop after 100 hours of storage in ambient air (RH ~ 40%) in comparison to control devices which exhibited a 19% of PCE drop. We will discuss the underlying structural-property relationship of how these fluorosilanes decorate and passivate the perovskite active layer.

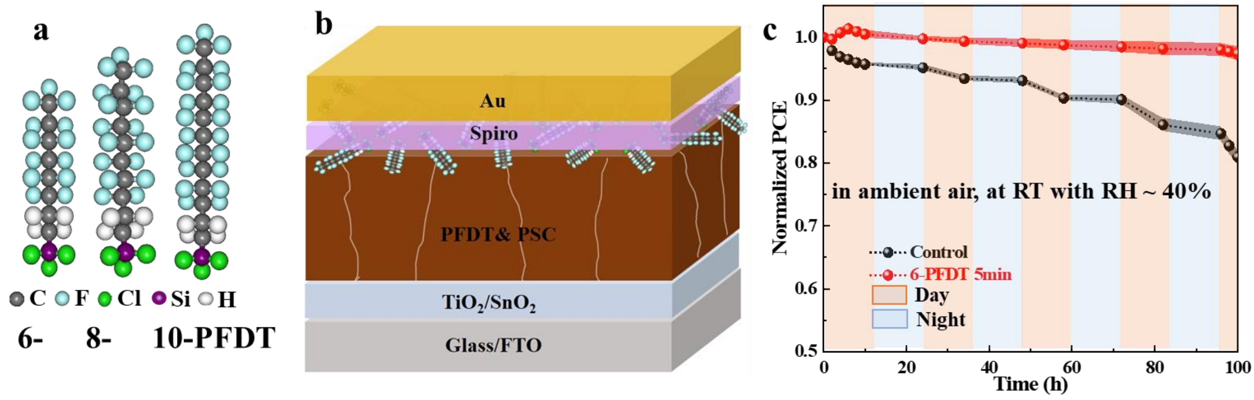

Figure 1. (a) Molecular structure of three PFDT with different perfluorocarbon chains. (b) Schematic device structure of PFDT-modified PSCs adopted in this work. (c) The stability of optimized decorated device and control device kept in ambient air (~25℃, HR~40%).

	Wednesday March 19th	Thursday March 20th	Friday March 21st
09:00		*Invited (40 minutes)* SAUVAGE Frédéric ALOUI M. A. CARRERIC K.	*Invited (40 minutes)* CHEN Zhuoying BALKIS N. ERTAY H.
10:20		*Break (30 minutes)*	*Break (30 minutes)*
10:50		PIRZADO A. A. A. *Invited (40 minutes)* GROS D'AILLON Eric CAI Y. HOANG T. H.	SOTO A. *Invited (40 minutes)* NGUYEN Hai Son XU Zeli DELPORT G.
12:30		*Lunch (1h30)*	*Lunch & Participant departures*
14:00	*Welcome of participants*	*Invited (40 minutes)* ABHERVÉ Alexandre GONG S. CHAMBISSIE KAMENI A. *Break (30 minutes)* JIANG J. CORBEL C. MANIADI M.	
15:30	*Tutorial (1 hour)* CACOVICH Stefania *Break (1 hour)* *Tutorial (1 hour)* VOLONAKIS George Break (30 minutes)		
16:50		*Poster session (2h40) & GDR Scientific Council*	
19:00	*Dinner (1h30)*		
19:30		*Dinner (1h30)*	
20:30	*Plenary session (1 hour)* BODNARCHUK Maryna		