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Avec le support de :

Session 1

Synthèse et propriétés fondamentales

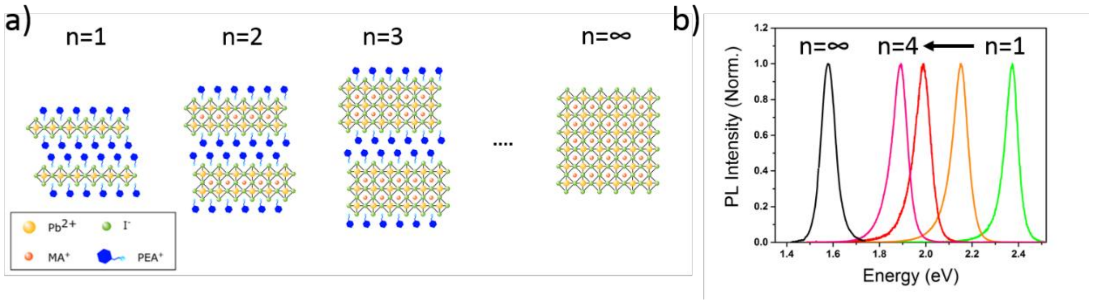
Exciton dynamics and trapping in 3D and 2D hybrid perovskites

D. Garrot,[1] *G. Chehade,*[2] *J. Urban,*[2] *G. Delport,*[3] *G. Allard-Trippé,*[2] *Aymeric Delteil,*[1] *Jean-Pierre Hermier,*[1]
J.-S. Lauret,[2] *E. Deleporte*[2]

1. Université Paris-Saclay, UVSQ, CNRS, GEMaC, 78000, Versailles, France
2. LuMIn, Université Paris-Saclay, ENS Paris-Saclay, CNRS, Centrale Supelec, 91405 Orsay, France
3. CNRS, Ecole Polytechnique UMR 9006, Institut Photovoltaique d'Ile de France (IPVF), Palaiseau, France

Halide perovskites present a great potential for optoelectronics devices such as solar cells, laser, light-emitting diodes and photodetectors. For further optimization of the devices, a deeper understanding of their intrinsic photophysical properties is highly desirable. The nature and impact of defects on the recombination dynamics are important parameters. Ruddlesden-Popper hybrid Perovskites (RPPs) present the general formula $(RNH_3)_2(MA)_{n-1}A_nX_{3n+1}$where MA = CH_3NH_3 and R is an alkyl or aromatic group, M a metal, and X a halide (Figure 1a). They self-assembled in a natural quantum well structure, where n perovskite layers are sandwiched between large organic cations. The optoelectronic properties can be tuned by increasing the number of inorganic layers from 2D to 3D ($n = \infty$) (Figure 2b). We have investigated the recombination dynamics and the role of trap states in crystals of the 3D perovskite $CH_3NH_3PbI_3$ (MAPI) and 2D RPPs using time-resolved and temperature dependent micro-photoluminescence (PL).

The room temperature emission of MAPI is dominated by the recombination of free carriers. However, at low temperature, the emission of the free exciton can be observed in high quality crystals and its interaction with phonons studied.[1] The nature of the low temperature multi-peak emission of MAPI is still debated. Based on micro-PL measurements on MAPI crystals, we are able to separate the different contributions. We have investigated the substructure of the defect emission of MAPI at low temperature. The observations provide a deeper insight on the nature of trap states in hybrid perovskites.



Figures 1: a) Schematic representation of the Ruddlesden-Popper hybrid perovskites b) Photoluminescence for different n values at room temperature

Contrary to MAPI, the excitonic properties of 2D RPPs can be studied at room temperature. [2] We have studied the recombination dynamics over a broad range of power excitation in 2D RPPs based on different organic cations: phenethylammonium (PEA), para-fluorophenethylamonium (4FPEA) and butylammonium (BA). We have developed a kinetic model based on a global analysis of the power-dependent PL decays. The results highlight the effect of exciton trapping on the dynamics. We have focused on the description of the long lived component of PL decays in 2D RPPs, whose possible origin is discussed.

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Hybrid lead-iodide perovskite materials for photovoltaic applications

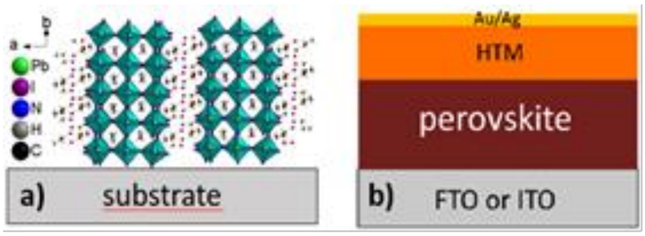
Alla Skorokhod,[a] Nicolas Mercier[a]

a) Laboratory MOLTECH-Anjou, UMR 6200 CNRS, Université d'Angers, Faculté des Sciences, 2 Boulevard Lavoisier, Angers

Hybrid lead-halide perovskites stand among the most promising photoactive materials because of their excellent physical properties including strong absorption coefficients, high mobility, and long carrier lifetimes.[1] The recently achieved perovskite solar cells have a record efficiency of 25,5%.[2] However, the lead-based perovskites have two major disadvantages as toxicity[3] and low stability, which have raised considerable concerns for their real applications. They are not stable under the influence of such factors as heat, humidity, and light soaking.[4] Therefore, most recent efforts have been focused on the design of novel stable hybrid two-dimensional (2D) perovskite by introduction new hydrophobic organic cations.[5]

The hydrophobic layers of big organic cations in 2D structures protect the inorganic framework from the moisture, that significantly improves the stability of hybrid perovskite material.[6] In photovoltaic devices perovskites functions not only as light absorbers but also as charge-transfer material. However, only inorganic network of perovskite lattice performs conducting properties and organic layers act as electron insulator.[7] Therefore, the vertical orientation **(a)** of metal halide framework in the thin films of 2D perovskites plays important role in solar cells fabrication **(b)**.

Here, we reported a family of lead-iodide 2D multi-layered Ruddlesden–Popper hybrid perovskites with the general formula $(I\text{-}R\text{-}NH_3)_2\,(CH_3NH_3)_{n-1}[Pb_nI_{3n+1}]$ (R – alkyl chain, n – number of layers). The structural aspect, optical properties, thin-film formation and stability of these new phases will be discussed.



***a)** Schematic illustration of vertical orientation of 2D perovskites in thin films; **b)** example of device architecture for perovskite solar cell*

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Electrodeposition of Perovskites for Large Surface Solar Devices: Impact of Deposition Parameters, Substrate Nature and Conversion Route.

Mirella Al Katrib [1], *Lara Perrin* [1, *], *and Emilie Planes* [1, *]
[1] *Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France*

Hybrid organic/inorganic perovskite solar cells have emerged substantially in the solar community, and are considered as a remarkable alternative because of its low cost and its efficiency's fascinating rise in the last ten years[1]. Spin coating is so far the most used technique for elaborating perovskite active layers, though it presents many constraints such as limited surface coverage, non-homogeneity, and undefined perovskite crystallinity. To avoid all the restrictions mentioned, electrodeposition could be used as an alternative[2]. Herein, electrodeposition of PbO_2 was used as a first step to elaborate controlled $CH_3NH_3PbI_3$ perovskite layers. Then, conversion of PbO_2 films into perovskite was conducted either by direct immersion in CH_3NH_3I solution, or by conversion into PbI_2 before immersion in CH_3NH_3I solution. In this work, the impact of different electrodeposition parameters on both PbO_2 and perovskite films was studied. The main interfering parameters are the applied voltage, electrodeposition time, the concentration and the pH of the electrolyte. An effect of the substrate nature was also observed by conducting the study on both "Glass/ITO" and "Glass/ITO/SnO_2" substrates. Cyclic voltammetry, chronocoulometry, profilometry, UV-visible spectroscopy, photoluminescence spectroscopy, X-Ray Diffraction and Scanning Electron Microscopy were all used to optimize the deposition parameters. In addition, the impact of each conversion route was evaluated by comparing the efficiencies in a "Glass/ITO/SnO_2/$CH_3NH_3PbI_3$/P3HT/Carbon" solar cell, having an active surface of 0.25 cm^2. While the efficiency for directly converted perovskite films is negligible, it reaches 3.3% when using a two-step conversion. This opens the way to promising performances using electrodeposition.

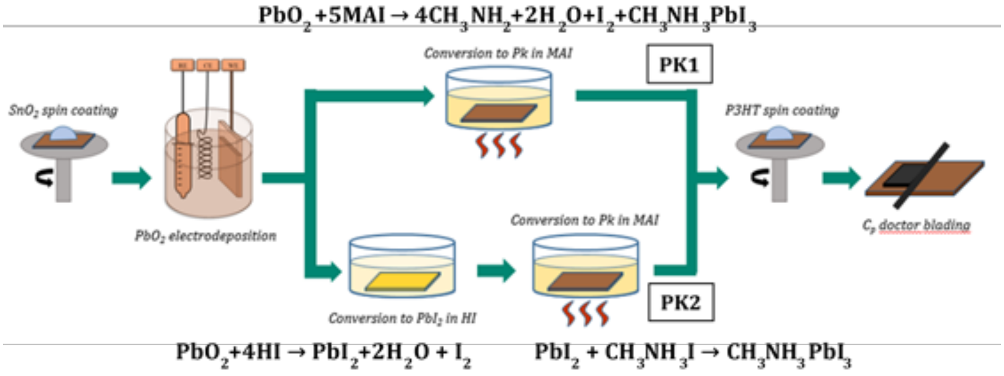

Figure 1: Diagram showing the consecutive steps for elaborating the solar cell

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Pérovskites sans plomb encapsulées dans les matrices mésoporeuses

Dmitry Aldakov,[1] *Andrey Ryzhikov*[2]

[1] Univ. Grenoble Alpes, CEA, CNRS, IRIG-SyMMES UMR-5819, 38000 Grenoble
[2] Univ. Haute Alsace UHA, Inst Sci Mat Mulhouse IS2M, CNRS, UMR 7361, 68100 Mulhouse

Les pérovskites halogénées à base du plomb ont récemment émergé comme une nouvelle classe de matériaux très prometteurs pour l'optoélectronique et photovoltaïque grâce à leurs propriétés uniques couplées à la fabrication peu chère et facile. De plus, les rendements quantiques (QY) de photoluminescence (PL) élevés et bandes d'émission étroites montrent leur fort potentiel pour utilisation en tant qu'émetteurs de lumière. Les nanocristaux (NCx) de pérovskites permettent d'améliorer les performances de ces matériaux grâce au confinement quantique et le contrôle de surface ce qui a récemment mené au PLQY de 100% obtenu pour les NCx de $CsPbI_3$.[1] Des méthodes classiques de synthèse utilisent des ligands de surface pour stabiliser les NCs en solution ce qui complique leur intégration directe dans les dispositifs finaux. Une des possibilités d'améliorer la stabilité des pérovskites tout en évitant l'utilisation des ligands est leur encapsulation dans les matrices nanoporeuses. Ces hôtes avec une porosité ordonnée permettent de contrôler la taille et la forme des NCx tout en protégeant leur surface naturellement. Des premiers exemples de pérovskites encapsulées dans les matrices nanoporeuses n'ont commencé à apparaître que très récemment,[2,3] et une possibilité d'intégrer ces nanomatériaux dans les LEDs efficaces a été démontrée.[4]

Dans ce travail nous démontrons le développement des nanocomposites de pérovskites sans plomb dans les silices mésoporeuses (SBA-15, taille des pores 4-8 nm). Pour la première fois, nous avons synthétisé des NCx de $MA_3Bi_2Br_3$ avec les tailles de 3-7 nm dans les pores de matrices mésoporeuses en utilisant la synthèse *in situ* dans les hôtes avec l'échange cationique ou l'imprégnation des solutions des pérovskites préparées *ex situ* (Fig. 1). Les spectres d'absorption et de PL de NCx se décalent en fonction de la taille des pores ce qui démontre une présence du confinement quantique. Les matériaux obtenus ont été caractérisés par des méthodes physicochimiques et structurales.

Ces nanocristaux confinés présentent une plateforme idéale pour étudier les propriétés fondamentales de plusieurs perovskites, y compris l'énergie de liaison d'excitons, dépendance de la structure des pérovskites sur la taille des cristallites etc. Enfin, ces matériaux seront testés comme phosphores prometteurs pour les émetteurs LED ayant la stabilité et efficacité de PL élevées ainsi que la faible toxicité.

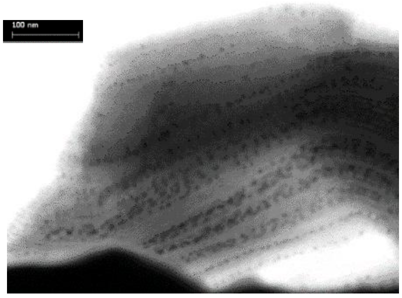

Figure 1. Image STEM de $MA_3Bi_2Br_9$ encapsulé dans la matrice de SBA-15.

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Dépôt sous-vide de couches minces de pérovskites hybrides : mode de croissance et structure cristalline

H. Khemliche [a], E. M. Staicu Casagrande [a], A. Momeni [a], A. Allouche [a], E. Deleporte [b], G. Trippé-Allard [b],
J. S. Lauret [b], D. Garrot [c]

[a] Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405, Orsay, France
[b] Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupélec, Laboratoire Lumière, Matière et Interfaces, 91405, Orsay, France
[c] Université Paris-Saclay, UVSQ, CNRS, GEMaC, 78000, Versailles, France

Les pérovskites hybrides organiques-inorganiques, qui ont permis d'atteindre en quelques années des rendements photovoltaïques records, souffrent cependant d'une stabilité médiocre provenant au moins en partie du caractère poreux des couches minces fabriquées quasi-exclusivement par voie humide. Afin d'améliorer la qualité de ce matériau, plusieurs tentatives d'élaboration sous vide ont déjà été menées, avec des résultats positifs en ce qui concerne leurs qualités morphologiques [1]. Nous proposons d'aller plus loin dans le contrôle de croissance de ces couches minces en exploitant la capacité de GIFAD (Grazing Incidence Fast Atom Diffraction) à fournir en temps réel des informations très détaillées sur le mode de croissance, les propriétés cristallines ainsi que les éventuelles transitions de phase [2]. La sensibilité de cette technique, développée à l'ISMO et dont la pertinence a déjà été démontrée récemment sur la dynamique de cristallisation d'une monocouche organique [3], devrait permettre l'élaboration de couches de très bonne qualité tout en apportant une meilleure compréhension de la transition de phase tétragonale-cubique observée au-dessus de 50°C.
Nous présenterons les premiers résultats de cette approche, en particulier les propriétés structurales d'une monocouche de $CH_3NH_3PbI_3$ épitaxiée sur un monocristal d'argent (figure 1).

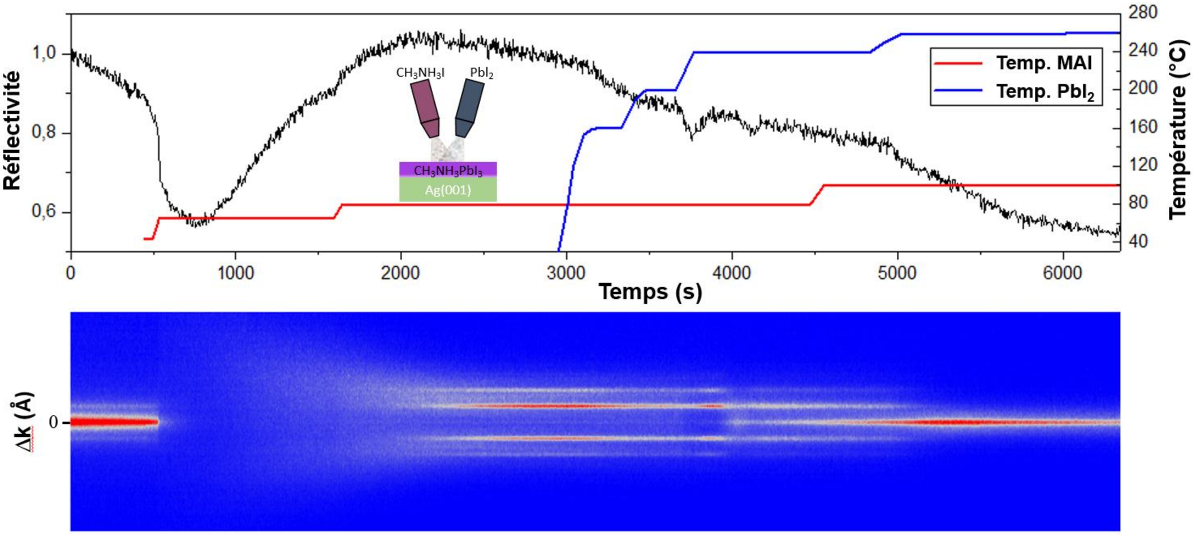

Figure 1. *Evolution de la réflectivité de la surface en cours de croissance, la températures d'évaporation des composants est indiquée à droite. Le pic de réflectivité vers 2200s signe la complétion d'une couche cristalline, impliquant uniquement le CH_3NH_3I, mouillant parfaitement le substrat. L'apport de PbI_2 induit plusieurs transitions de phase avec, en fin de dépôt (non visible ici), une structure hexagonale non commensurée sur le substrat.*

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Triphenylamine/Thieno[3,4-c]pyrrole-4,6-dione based D–π-A–π-D Dyes: Synthesis, Characterization and Photovoltaic Applications

Thi Huong Le,[1] Seul-Gi Kim,[2] Thybault de Monfreid,[1] Fabrice Goubard,[1] Nam-Gyu Park,[2] Thanh-Tuân Bui[1]*[+]*
[1]CY Cergy Paris Université, LPPI, F-95000 Cergy, France. E-mail: tbui@cyu.fr
[2]School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon 440-746, Korea. Email: npark@skku.edu
[+]Presenting author

We report here the design and synthesis of a series of conjugated molecules based on thieno[3,4-c]pyrrole-4,6-dione central core in a D–π-A–π-D molecular configuration for perovskite solar cells application. The thermal, morphological, optical and electrochemical properties of all prepared compounds have been investigated in detail and a comparative discussion has been presented.

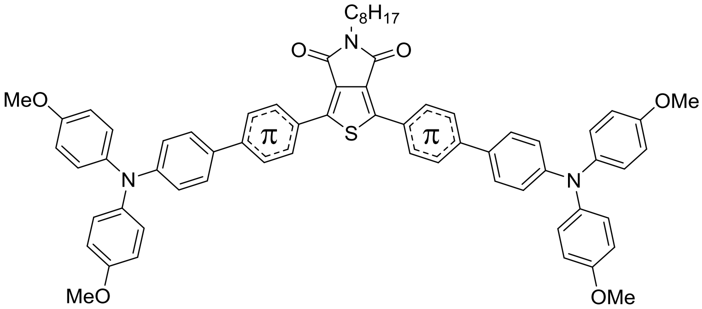

Figure 1. Molecular structures of investigated molecules

Their characteristics have suggested that these molecules could be suitable for use as hole transporting materials in perovskite photovoltaic devices. The preliminary photovoltaic application have given devices with power conversion efficiency (PCE) around 17 %. One of these molecules has been selected for further device optimization. Interface engineering with 2-(2-aminoethyl)thiophene hydroiodide (2-TEAI) between perovskite and hole transport layers improves PCE from 19.60% (untreated) to 21.98% (treated) and this champion PCE is even higher than that of the spiro-MeOTAD-based device (21.15%). Thermal stability test at 85 °C for over 1000 h showed that the PSC employed novel HTM retains 85.9% of initial PCE (from 21.9% (0 h) to 18.8% (1032 h)), while the spiro-MeOTAD-based PSC degrades unrecoverably from 21.1% to 5.8%. Time-of-flight secondary ion mass spectrometry studies combined with Fourier transformed infrared spectroscopy reveal that novel HTM shows much lower lithium ion diffusivity than spiro-MeOTAD due to a strong complexation of the lithium ion with HTM, which is responsible for the higher degree of thermal stability. This work delivers an important message that capturing mobile Li^+ in hole transporting layer is critical in designing novel HTM for improving thermal stability of PSCs. In addition, it also highlights the importance of interfacial engineering on the non-conventional HTM.

KEYWORDS: perovskite solar cell, hole transporting material, interface engineering, thermal stability, conjugated materials, push-pull dyes

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Capturing Mobile Lithium Ion in Molecular Hole Transporter Enhances Thermal Stability of Perovskite Solar Cells.
S.-G. Kim, T. H. Le, T. de Monfreid, F. Goubard, T.-T. Bui,* N.-G. Park* *Adv. Mater.* **2021** *(Accepted 12/01/2021).* https://doi.org/10.1002/adma.202007431

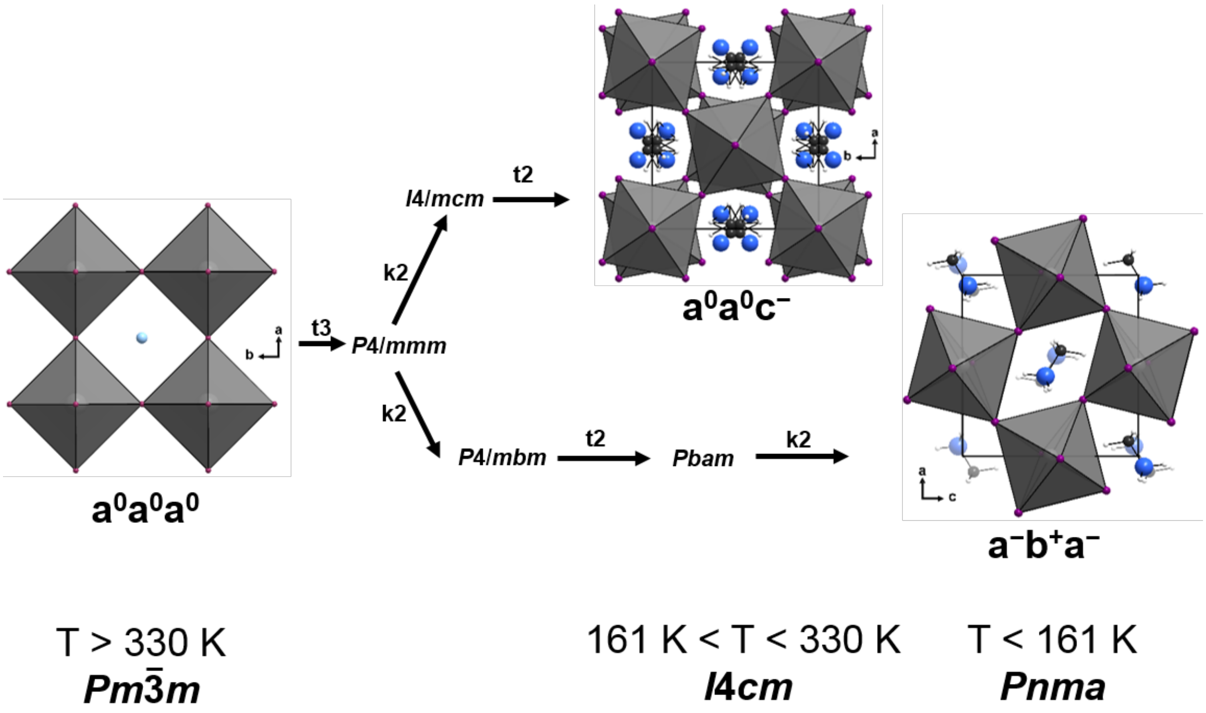
Une étude structurale systématique pour les pérovskites halogénées

Joachim Breternitz,[1,2] *Susan Schorr*[1,3]
1 Helmholtz-Zentrum Berlin für Materialien und Energie, Department Structure and Dynamics of Energy Materials, 14109 Berlin
2 Universität Potsdam, Institute for Chemistry, 14476 Potsdam
3 Freie Universität Berlin, Department Geosciences, 12249 Berlin

L'efficacités des cellules solaires utilisant des pérovskites halogénées atteint désormais 25,5 %,[1] proche de leur limite théorique telle que calculée par Schockley-Queisser.[2] Les efforts de recherche dévoués à la compréhension fondamentale de ces matériaux sont importants mais restent en retrait vis-à-vis de ceux focalisés sur l'augmentation des rendements.

La famille des pérovskites comporte plusieurs structures cristallines,[3] qui dépendent de la composition mais aussi de paramètres environnementaux (tels que la température et la pression). Cependant le terme « pérovskite » est parfois employé abusivement pour des matériaux dont la structure cristalline est « dérivée de » mais pas « rigoureusement » pérovskite.[4] Les propriétés des matériaux étant gouvernées par leur structure cristalline, la distinction est cependant cruciale au-delà de la communauté des cristallographes.

Dans cette présentation, nous allons d'abord présenter les relations entre les structures cristallines de la famille des pérovskites et leur classification systématique par sous-groupe sous forme d'arbre de Bärnighausen. Nous illustrerons dans un second temps la pertinence de cette approche en montrant qu'elle permet d'expliquer certaines propriétés structurales (maclage, compréhension des transitions de phase, ferroélasticité) et électroniques (ferroélectricité).



Figures 1 : Représentation de la relation groupe – sous-groupe pour les différentes phases de $MAPbI_3$.

[1] *https://www.nrel.gov/pv/cell-efficiency.html*, accédé 23/02/2021.
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Polymorphisme dans les pérovskites halogénées à base de formamidinium : au-delà du facteur de tolérance

Asma A. Medjahed[1]*, David Djurado*[1]*, Peter Reiss*[1]*, Stéphanie Pouget*[2]
[1] *Univ. Grenoble Alpes, CEA, CNRS, IRIG/SyMMES/STEP, 38000 Grenoble*
[2] *Univ. Grenoble Alpes, CEA, IRIG/MEM, 38000 Grenoble*

Grâce à son énergie de bande interdite E_g plus proche de la valeur optimale dans la limite de Shockley-Queisser (1,34 eV), le composé de structure cubique pérovskite $FAPbI_3$ (FA = formamidinium, E_g = 1.48 eV) promet des efficacités en cellule solaire supérieures à celles atteintes par les dispositifs à base de $MAPbI_3$ (MA = méthylammonium, E_g = 1.55 eV). Toutefois, l'utilisation de $FAPbI_3$ a grandement été freinée par le caractère métastable de sa phase cubique à température ambiante (TA). En effet, après synthèse à haute température (HT), ce composé évolue spontanément avec une cinétique variable vers une phase hexagonale à large bande interdite, la phase cubique n'étant stable qu'à HT. Une voie largement utilisée pour stabiliser la phase pérovskite cubique à TA consiste à former des solutions solides telles que $Cs_xFA_{1-x}Pb(I_{1-z}Br_z)_3$ ou $Cs_yFA_{1-x-y}MA_xPb(I_{1-z}Br_z)_3$, l'influence des différents ions dans cette stabilisation restant méconnue. De plus, la question du polymorphisme de $FAPbI_3$ n'est pas résolue, la plupart des travaux attribuant cette instabilité simplement à un facteur de tolérance supérieur à 1. Le facteur de tolérance, uniquement basé sur le rapport des rayons ioniques de la structure, définit une condition géométrique de stabilité de la phase pérovskite cubique et prédit la formation d'une structure hexagonale pour les valeurs supérieures à 1. Cependant, les composés $FAPbBr_3$ et $FAPbCl_3$ ont tous les deux des facteurs de tolérance supérieur à 1 mais adoptent une maille cubique stable à TA.

Nous présenterons ici nos travaux autour de la substitution graduelle des ions iodures par les ions bromures dans le $FAPbI_3$. Nous montrerons que l'insertion de brome dans la structure ne stabilise la phase cubique à TA que pour de fortes compositions en brome (60% et plus), alors que pour des faibles pourcentages (entre 10 et 20 %), ce sont d'autres polymorphes hexagonaux qui sont formés (Figure 1). Pour des compositions en brome intermédiaires (entre 30% et 50%), il apparaît impossible de stabiliser une structure cubique dans le domaine en température exploré (jusqu'à 200 °C). Couplé à un suivi de l'effet de la substitution du FA^+ par du MA^+ sur les propriétés structurales des composés obtenus, nos travaux suggèrent l'influence non négligeable de la répulsion électrostatique [1] dans la stabilisation de la phase cubique dans les pérovskites hybrides halogénées.

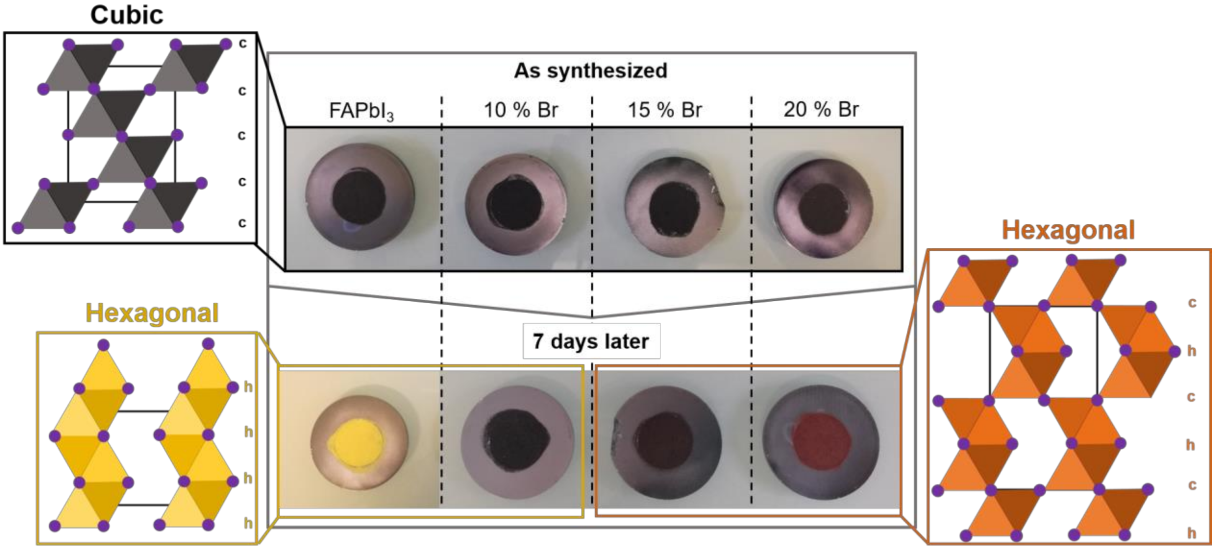

Figure 1 : Evolution spontanée des composés $FAPb(I_{1-x}Br_x)$ pour x = 0, 10, 15 et 20% en leur polymorphes hexagonaux stables à température ambiante.

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Optical properties of a mixed perovskite (FAPbI3)1-x(MAPbBr3)x thin Films Synthesized by Spin Coating Process for Solar Cells

B. Slimi[a,b], *B. Marí*[a], *R. Chtourou*[b]

[a] *Institut de Disseny i Fabricació, Universitat Politècnica de València, Camí de Vera s/n, 46022 València, SPAIN*
[b] *Laboratory of Nanomaterials and Systems for Renewable Energies (LaNSER), Research and Technology Centerof Energy, Techno-park Borj-Cedria,Bp95, Hammam-Lif 2050, Tunis, Tunisia*

This paper presents the study of a coating technique for Perovskite material in order to elaborate thin films for solar cells applications. In the following work a spin coating technique was used for $FAPbI_3$, $MAPbBr_3$ and $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ perovskites thin films were produced in a single step from a solution containing a mixture of FAI, MABr, PbI_2 and $PbBr_2$ (FA=Formamidinium, MA=Methylammonium) in DMF. The perovskite thin films were deposited onto ITO-coated glass substrates by spin coating. X-ray diffraction analyses confirmed that these thin film perovskites crystallize in the cubic phase (Pm-3m) for all composition range. Mixed lead perovskites showed a high absorbance in the UV–vis range. The optical band gap was estimated from spectral absorbance measurements. It was found that the onset of the absorption edge for thin films ranges between 1.47 and 2.23 eV for $FAPbI_3$ and $MAPbBr_3$, respectively. Photoluminescence emission energies for the perovskites were also dependent on their composition and presented intermediate values from 810.4 nm for $FAPbI_3$ to 547.3 nm for $MAPbBr_3$.

Keywords: Organic-inorganic perovskites, Formamidinium Lead Iodide, Methylammonium Lead Bromide, X-Ray diffraction, Optical absorption, Photoluminescence.

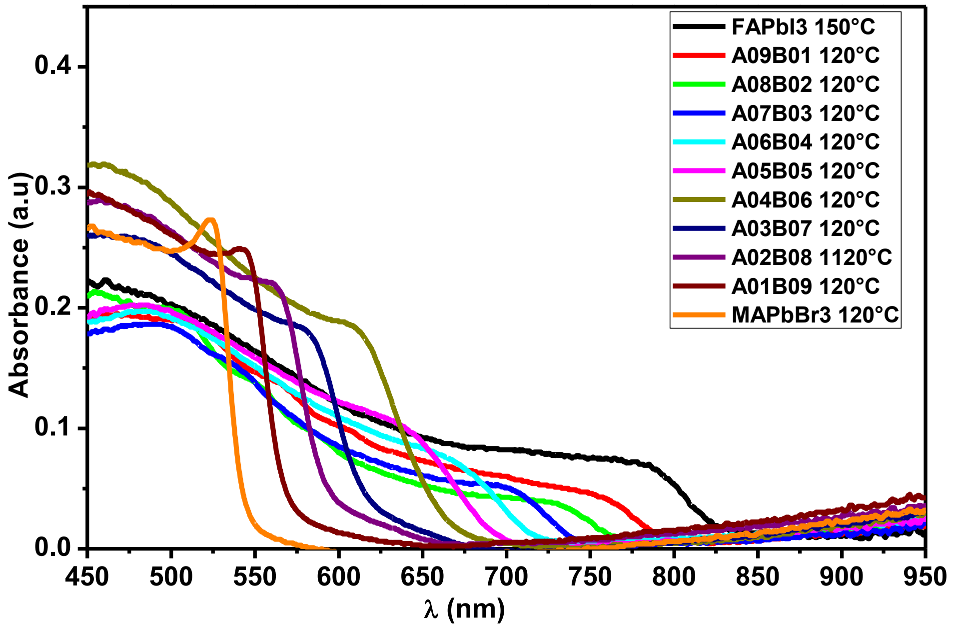

Figure *.The samples with different concentrations of MAI. The estimated band gap for all MAI concentrations for $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ is 1.50-156 eV.*

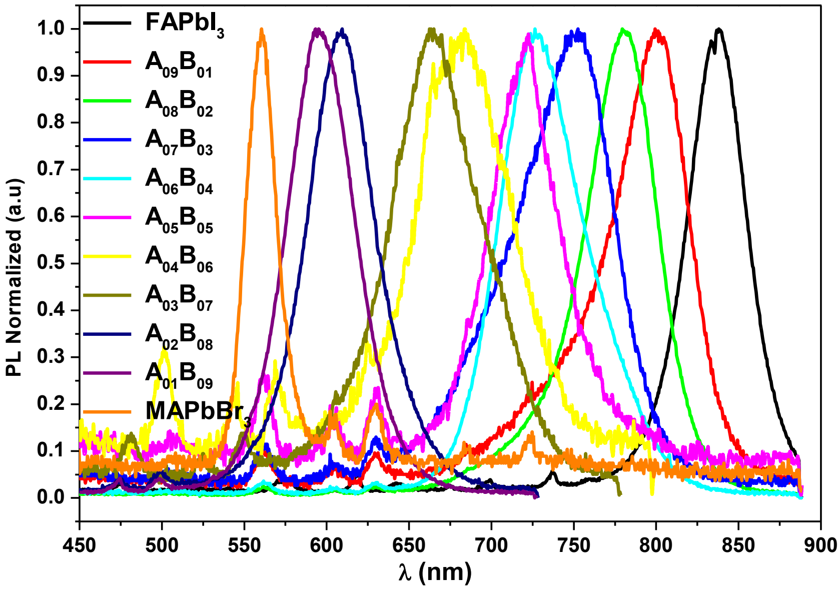

Figure . *Room photoluminescence spectra (PL) Normalized for $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ (x = 0, 0.1, 0.2, 0.4, 0.6,0.7, 0.8, 1) thin films.*

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Reversible nature of photo-induced phase segregation and origin of long carrier lifetime in triple cation mixed halide perovskite films

Subodh K. Gautam[1,*], *Minjin Kim*[2], *Douglas R. Miquita*[1,3], *Jean-Eric Bouree*[2], *Bernard Geffroy*[2,4] *and Olivier Plantevin*[1]

1 Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405, Orsay, France.
2 LPICM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, route de Saclay, 91128 Palaiseau, France.
3 Centro de Microscopia - Universidade Federal de Minas Gerais, Belo Horizonte, MG, 31270-901- Brasil
4 Université Paris-Saclay, CEA, CNRS, NIMBE, LICSEN, 91191, Gif-sur-Yvette, France

Mixed-halide based hybrid perovskite semiconductors have attracted tremendous attention as a promising candidate for high efficient photovoltaic and light-emitting devices [1]. However, these advanced perovskite materials may undergo phase-segregation under light illumination due to halide ion migration and affecting their optoelectronic properties [2, 3]. In this contribution, we report such phase segregation effect in triple-cation mixed-halide perovskite film when subjected to photo-excitation and quantitatively analyze the processes that occur during phase segregation [4]. We highlight the relationship between photo-induced phase segregation and unusual increase in carrier lifetime in mixed halide perovskite under illumination (> 1 μs). Laser excitation induced halide ion migration lead to formation of smaller-bandgap iodide-rich and larger-bandgap bromide-rich domains which yield to red-shift in photoluminescence. The segregated iodide-rich domains efficiently trap the photo-excited-carriers where they are long lived before recombination, revealing their dominant role in the origin of the unusual long carrier lifetime. Interestingly, these photo-induced changes are fully reversible and thermally activated when laser-excitation is turned off measured in temperature range of 270K-330K. A significant difference in activation energies for halide ion migration is observed during photo-excitation and recovery process under dark. In addition, temperature-dependent PL studies (10 K - 300 K) have been performed for better understanding of the role of exciton–phonon coupling to interpret the phase segregation driving forces. These findings will help to understand the key issues in the perovskite materials for the development of efficient solar cells and optoelectronic devices.

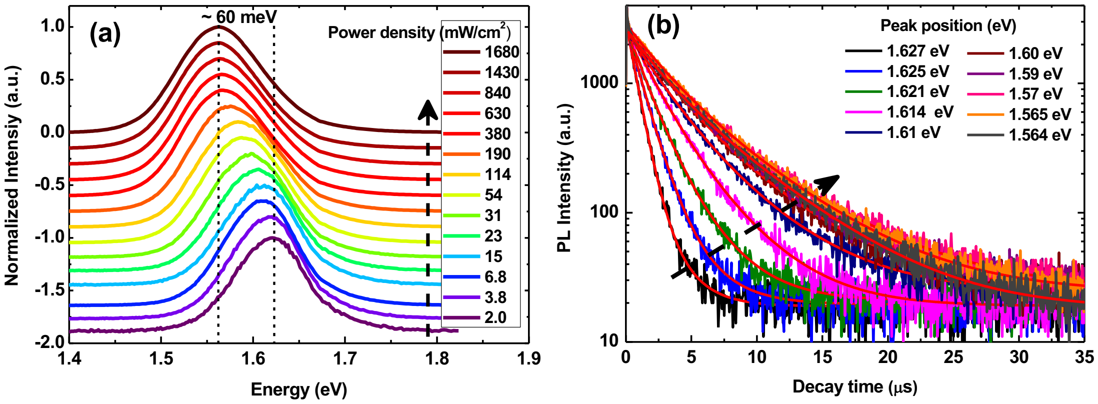

Figure: (a) Laser power-dependent photoluminescence (PL) spectra of triple-cation mixed-halide $(MA_{0.83}FA_{0.17})_{0.95}Cs_{0.05}Pb(I_{0.83}Br_{0.17})_3$ perovskite film showing red-shift in PL at room temperature and **(b)** PL-decay spectra measured on red-shifted PL positions.

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Solutions solides de pérovskites hybrides halogénées : propriétés intrinsèques à l'ambiante et comportement en température

Asma A. Medjahed[1], *David Djurado*[1], *Peter Reiss*[1], *Stéphanie Pouget*[2]
[1] *Univ. Grenoble Alpes, CEA, CNRS, IRIG/SyMMES/STEP, 38000 Grenoble*
[2] *Univ. Grenoble Alpes, CEA, IRIG/MEM, 38000 Grenoble*

La dégradation rapide lorsqu'exposées des couches minces $MAPbI_3$ (MA = methylammonium) à l'oxygène, à l'humidité ainsi qu'à la lumière a mené la communauté scientifique à développer de nouveaux matériaux pour les dispositifs photovoltaïques. Plusieurs stratégies sont employées à ce jour, parmi lesquelles l'utilisation de solutions solides multi-cations organiques et multi-halogènes, telles que $Cs_xFA_{1-x-y}MA_xPb(I_{1-z}Br_z)_3$ ou encore $Cs_xFA_{1-x}Pb(I_{1-z}Br_z)_3$ (où FA = formamidinium). Ces composés ont mené à des dispositifs plus stables et présentant des efficacités supérieures aux dispositifs à base de $MAPbI_3$. Ainsi la synthèse du matériau complexe $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$ et son utilisation comme matériau actif en cellules solaires nous a permis d'atteindre des efficacités allant jusqu'à 21.75% [1]. Alors que les principaux enjeux technologiques autour de ces matériaux sont de maitriser les inhomogénéités de composition observées dans les couches minces, de nombreuses questions se posent encore par rapport à leurs propriétés intrinsèques, notamment structurales.

Notre approche consiste, en partant des composés ternaires $MAPbI_3$, $FAPbI_3$, $MAPbBr_3$ et $FAPbBr_3$ à substituer un site ionique à la fois, générant ainsi les trois familles de composés quaternaires $MAPb(I_{1-x}Br_x)_3$, $FAPb(I_{1-x}Br_x)_3$ et $FA_{1-x}MA_xPbI_3$. En adaptant les conditions de synthèse des échantillons sous forme de poudre, une solubilité complète dans les séries $MAPb(I_{1-x}Br_x)_3$ et $FAPb(I_{1-x}Br_x)_3$ a été obtenue, contrastant avec des travaux existants [2]. Il apparaît que malgré les fortes distorsions de la structure induites par le mélange des halogènes dans ces composés, les paramètres de maille obtenus suivent la loi de Vegard. La spectroscopie d'absorption UV-Vis montre par ailleurs que l'énergie de la bande interdite évolue linéairement en fonction de la composition. Des études de diffraction de rayons X (DRX) réalisées à différentes températures entre 90 K et 400 K, révèlent des comportements en température singuliers des composés ternaires $FAPbI_3$ et $FAPbBr_3$; elles nous ont permis d'établir le diagramme de phase des deux familles $MAPb(I_{1-x}Br_x)_3$ et $FAPb(I_{1-x}Br_x)_3$ qui seront discutés et comparés à celui de la famille $FA_{1-x}MA_xPbI_3$ [3]. Nous présenterons ensuite les résultats de l'étude, par DRX et UV-Vis, du matériau $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$, utilisé en cellules solaires. Ils seront discutés à la lumière des résultats obtenus sur les composés quaternaires.

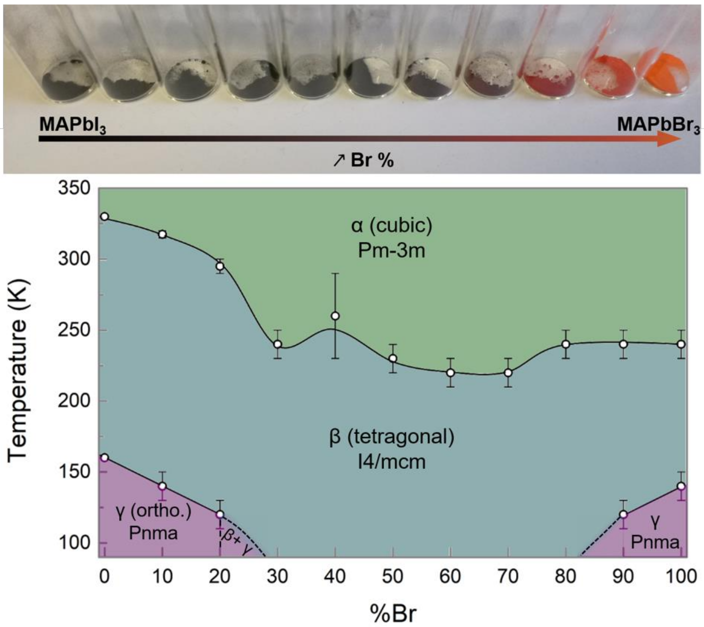

Figure 1 Photographie de composés $MAPb(I_{1-x}Br_x)_3$ avec une composition en brome croissante, montrant l'évolution de couleur des composés et attestant d'une modification graduelle de l'énergie de bande interdite. Diagramme de phase de cette famille de composés (évolution des températures de transition structurales en fonction de la composition en Br^-).

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Multiexciton dynamics in colloidal 2D perovskite nanoplatelets: Auger recombination and multiple exciton generation in the strong confinement regime

Carolina Villamil Franco[1], Benoît Mahler[2], Christian Cornaggia[1], Thomas Gustavsson[1] and Elsa Cassette[1]
[1] Université Paris Saclay, CNRS, CEA, Laboratoire Interactions, Dynamiques et Lasers (LIDYL), 91190 Gif-sur-Yvette, France ; [2] Université de Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622 Villeurbanne, France

Improving the understanding of multiple exciton interactions and dynamics in semiconductor nanostructures is mandatory for their successful use as photoactive materials in light convertors such as electroluminescent diodes, lasers, or single-photon sources. Here high-fluence and high-energy excitation effects are investigated in strongly confined two-dimensional (2D) lead iodide perovskite nanoplatelets (NPLs) using time-resolved photoluminescence and femtosecond transient absorption (TA) spectroscopy. Nonradiative Auger recombination (AR) is the dominant pathway for multiexciton recombination. Its dynamics are found to be subquadratic with the exciton density. Indeed, because of the limited exciton wave-function delocalization length, AR is limited by exciton diffusion in the 2D plane at moderate excitation fluence and takes place in several hundreds of picoseconds, with typical recombination rates on the order of 10^{-2} cm^2/s. At high excitation fluence leading to an average interexciton distance comparable with the exciton delocalization length, the measured "intrinsic" AR time is faster than 10 ps and independent of the NPL composition. The strong dependence of the AR rate on the interexciton distance allows us to identify the recombination resulting from multiple exciton generation, involving the reaction of "geminate biexcitons", upon excitation at low fluence with high-energy photons.

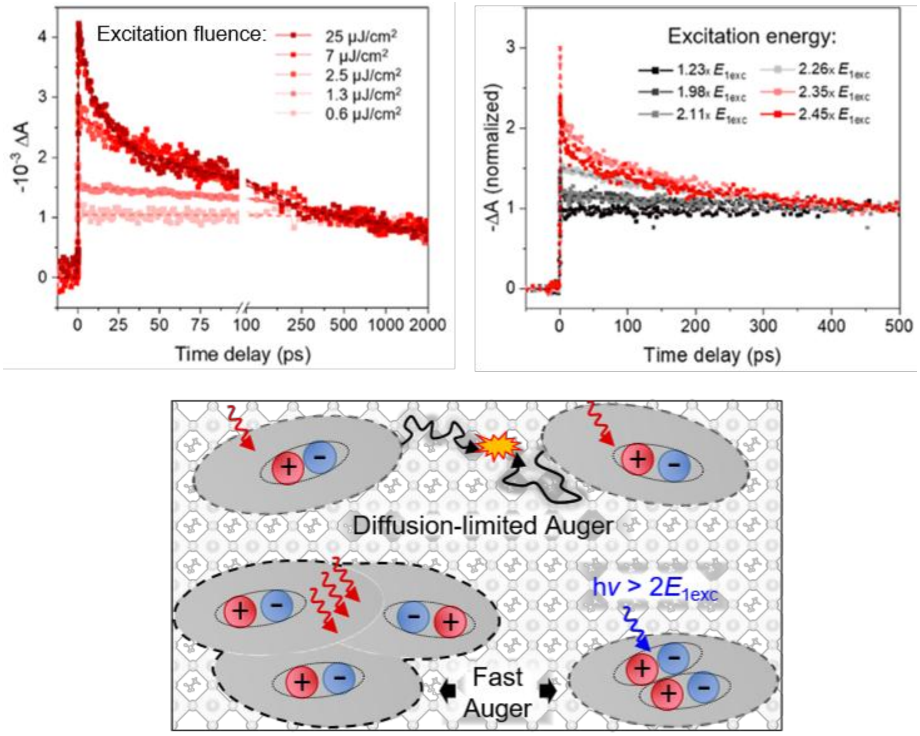

Figure 1. Top : TA decay traces of MAPI n=3 NPLs recorded at the bandedge bleach for a) different excitation fluences and b) various excitation energies (visible to UV) at low fluence. Bottom: Schematics of the interexciton distance effect on the AR rate depending on the experimental conditions.

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Magneto-spectroscopy studies provide direct evidence for the coupling of excitons to organic ligand vibrations in 2D RP perovskites

Joanna M. Urban[2], Gabriel Chehade[2], Mateusz Dyksik[1,3], Matan Menahem[4], Alessandro Surrente[1], Gaëlle Trippée-Allard[2], Duncan K. Maude[1], Damien Garrot[5], Omer Yaffe[4], Emmanuelle Deleporte[2], Paulina Plochocka[1] and Michal Baranowski[1,3]

[1]Laboratoire National des Champs Magnétiques Intenses, UPR 3228,CNRS-UGA-UPS-INSA,
Grenoble and Toulouse, France
[2]Laboratoire Lumière, Matière et Interfaces, Université Paris-Saclay, ENS Paris-Saclay, CNRS,
CentraleSupelec, 91405 Orsay Cedex, France
[3]Department of Experimental Physics, Faculty of Fundamental Problems of Technology,
Wroclaw University of Science and Technology, Wroclaw, Poland
[4] Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel
[5]Groupe d'Etude de la Matière Condensée, Université de Versailles Saint Quentin En Yvelines,
Université Paris-Saclay, 45 Avenue des Etats-Unis, 78035, Versailles, France

Layered Ruddlesden-Popper (RP) perovskites are promising candidates for optoelectronic applications due to their excellent stability and excitonic properties. These natural quantum well structures consisting of inorganic layers separated by large organic spacers have been known since several decades. However, only lately attention has turned towards investigating the distinctive nature of the exciton-phonon coupling as the driving mechanism for many of their unique properties [1].

In this work we show that despite the assumed confinement of the excitons withing the inorganic layers, for certain ligands significant coupling of the excitons to the vibrations of the organic part can occur. We investigated the RP perovskite $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (PEPI) [2] with a varying number of inorganic layers n=1,2,3 using magneto-transmission in magnetic fields up to 68 T [3]. In the transmission spectra we could identify periodically spaced features separated by around 40 meV which we assign as phonon replicas of the main excitonic transition. Our interpretation is strongly supported by the identical shifts of the features in magnetic field suggesting their common origin. The mode around 40 meV has been previously identified as the vibration of the PEA cation [1]. The observed coupling is an evidence of the leakage of the excitonic wavefunction into the organic barrier layer due to weaker dielectric confinement induced by the PEA cations as compared to alkyl chains.

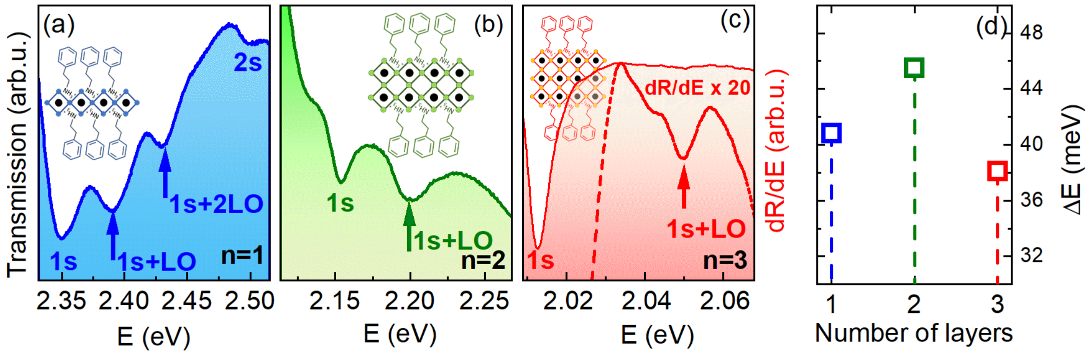

Fig.1 (a)-(c) Transmission spectra of the n=1,2,3 PEPI samples and (d) energetic separation of the 1s excitonic transition and the first phonon replica as a function of the number of inorganic layers.

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The Key Role of the Interface in the Highly Sensitive Mechanochromic Luminescence Properties of Hybrid Perovskites

Maroua Ben Haj Salah,[a] *Nicolas Mercier,*[a] *Jens Dittmer,*[b] *Nabil Zouari,*[c] *and Chiara Botta,*[d]

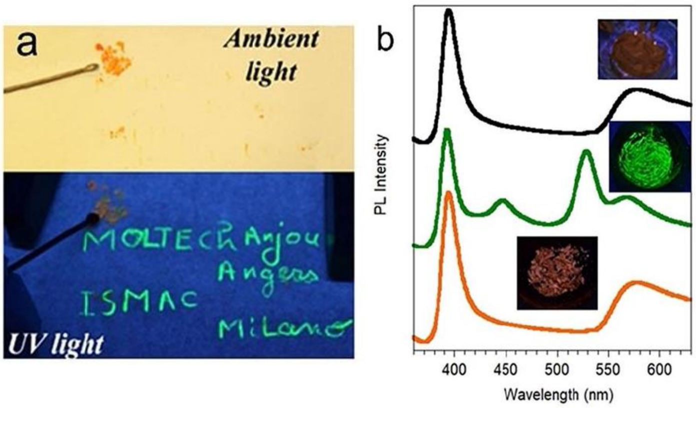
[a] *Laboratory MOLTECH-Anjou, UMR 6200 CNRS, Université d'Angers, Faculté des Sciences, 2 Boulevard Lavoisier, Angers*

[b] *Institut des Molécules et Matériaux du Mans,UMR CNRS 6283 Le MansUniversité AvenueOlivierMessiaen,72085Le Manscedex9(France)*

[c] *Laboratoire de Physico-chimiede l'état solide,Département de chimie,Faculté des sciences de Sfax,Université de Sfax 3000 Sfax (Tunisia)*

[d] *stitutodi Scienzee Tecnologie Chimiche,G. Natta"(SCITEC),CNR Via Corti 12, 20133Milano(Italy)*

Hybrid perovskite are attracting increasing attention among scientists because the molecular hybridization offers the potential of combining the best parts of characteristic properties of the two chemical entities as well as generating new properties arising from the molecular interactions between of two building block. Both 2D and 3D perovskites exhibiting specific electronic and optical properties related to their structural nature, represent a promising class of semi- conductors for photovoltaics[1] or lighting applications.[2] Here we report that hybrid perovskite composites, as crystallized powders, can behave as intelligent materials showing highly sensitive and reversible mechanochromic luminescence (MCL). Composites consisting of monolayer 2D HP and 3D HP components exhibit reversible tuneable colour emission upon mechanical strain. The bluish- whitish emission of the 2D HP turns into orange in the composite owing to an energy transfer process. The bright green emission, observed as soon as the composite is slightly crushed, originates from the 3D HP after efficient energy funnelling from the multi- layered 2D HP produced at the 2D/3D interface by the mechanical treatment (figures a and b). Besides highlighting the key role of the interfaces in light emission of HP, our findings pave the way for hybrid perovskites as highly sensitive MCL smart materials for mechanosensors, security papers, or optical storage applications.[3]



a) Message written by a spatula pen dipped into the pristine 2D- C4/3D composite orange appears green under UV light (bottom) while it is virtually invisible under ambient illumination (top). b) Process reversibility: PL spectra and photos of the pristine (bottom), crushed (middle) and crushed+acetone (top) samples.

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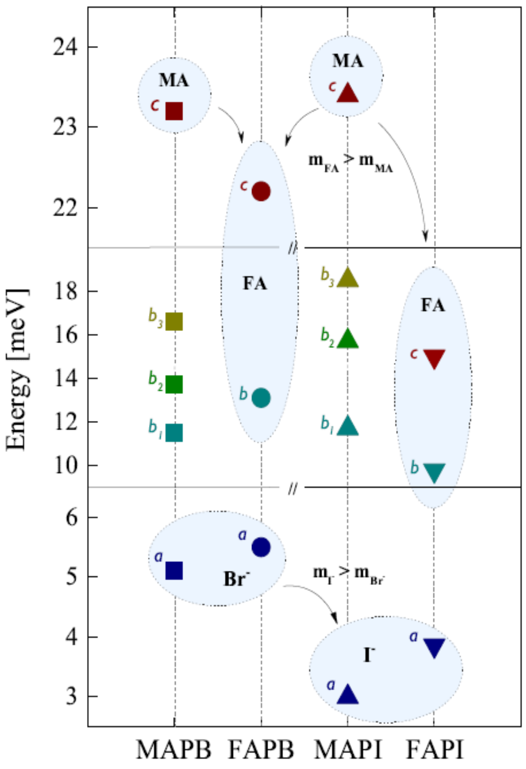
Direct evidence of weakly dispersed and strongly anharmonic low frequency optical phonons at low temperature in hybrid organolead perovskites

A.C. Ferreira[1, 2], S. Paofai[3], A. Létoublon[2], J. Ollivier[4], S. Raymond[5], B. Hehlen[6], B. Rufflé[6], S. Cordier[3], C. Katan[3], J. Even[2], and P. Bourges[1]

[1]Laboratoire Léon Brillouin, CEA-CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France
[2]Univ Rennes, INSA Rennes, CNRS, Institut FOTON - UMR 6082, F-35000 Rennes, France
[3]Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France
[4]Institut laue Langevin, 71 avenue des martyrs, 38000 Grenoble, France
[5]Univ. Grenoble Alpes, CEA, IRIG, MEM, MDN, F-38000 Grenoble
[6]Laboratoire Charles Coulomb, UMR 5221 CNRS-Université de Montpellier, Montpellier, FR-34095, France

Hybrid organolead perovskites (HOP) have started to establish themselves in the field of photovoltaics, mainly due to their great optoelectronic properties and steadily improving solar cell efficiency. Although much recent attention has been devoted towards unraveling their microscopic optoelectronic properties, the structural dynamics (phonons) are currently still lacking a comprehensive understanding as compared to that already reached for classic semiconductors. Study of the lattice dynamics is then a key in understanding the electron-phonon interactions at play, responsible for the electronic properties. Using inelastic neutron scattering and light (Brillouin and Raman) scattering, we have investigated the phonon spectrum in four different hybrid perovskite single crystals: $MAPbBr_3$, $FAPbBr_3$, $MAPbI_3$ and α-$FAPbI_3$, where MA and FA correspond to methylammonium (CH_3NH_3) and formamidinium ($(CH_2)_2NH$) molecules, respectively.



Previously, we have studied the low energy acoustic phonons and determine the complete set of elastic constants [1,2]. They are characterized by soft elastic constants compared to classic semiconductors, with a particular very soft shear modulus C_{44}. Between room temperature and 240 K, a tendency towards an incipient ferroelastic transition is also observed in FAPbBr3. A systematic lower sound group velocity is found in the technologically important iodide-based compounds compared to the bromide-based ones. The findings suggest that low thermal conductivity and hot phonon bottleneck phenomena are expected to be enhanced by low elastic stiffness, particularly in the case of the ultrasoft α-FAPbI3

Recently, we investigated the optical phonon spectrum below 40 meV in single crystals of the same four different hybrid lead halide perovskites [3]. Low temperature spectra reveal weakly dispersive optical phonons, grouped in three main bundles of phonons (see figure). These results will be discussed showing that the lowest energies phonons at 2-5 meV seem to be the origin of the limit of the charge carrier mobilities in these materials. The temperature dependence of the neutron spectra reveals a significant anharmonic behaviour, resulting in optical phonon overdamping at temperatures as low as 80 K, questionning the validity of the quasi-particle picture for the low energy optical modes at room temperature where the solar cells actually operate.

Figure: Main optical phonon bundles: *Energy positions of the three optical phonon bundles **a**, **b**, and **c**, between* MAPbBr3, FAPbBr3, MAPbI3, and *a*-FAPbI3. *The figure highlights the influence of the molecular and/or the halide component atomic masses on the associated optical phonon energy.*

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Ferroelasticité et contraintes dans les couches minces de MAPbI$_3$

Asma A. Medjahed[1], Tao Zhou[2], Pia Dally[3], Pascal Pochet[4], David Djurado[1], Peter Reiss[1], Stéphanie Pouget[4]
[1] Univ. Grenoble Alpes, CEA, CNRS, IRIG/SyMMES/STEP, 38000 Grenoble
[2] Argonne National Laboratory, Lemont, IL 60439, USA.
[3] IPVF, 91120 Palaiseau / ILV, 78035 Versailles
[4] Univ. Grenoble Alpes, CEA, IRIG/MEM, 38000 Grenoble

Le composé MAPbI$_3$ (MA = methylammonium) adopte une symétrie tétragonale à température ambiante, décrite par le groupe d'espace I4/mcm. La cristallisation de ce composé s'effectue le plus souvent à 100 °C, qu'il soit synthétisé sous forme de monocristal, de couche mince ou de poudre. Or, à cette température, MAPbI$_3$ est cubique (Pm-3m), il subit ainsi une transition de phase cubique-tétragonale lors de son refroidissement. Lors d'une telle transition, l'axe de symétrie d'ordre trois du cube est perdu, et l'élongation qui mène à la formation de la direction tétragonale c peut avoir lieu dans trois directions différentes, ce qui conduit à trois orientations équivalentes de la maille tétragonale (Figure 1.a)), et à l'apparition spontanée de macles. Cette transition de phase étant ferroélastique, l'application d'une contrainte mécanique extérieure permet de modifier l'orientation des domaines. Une étude par diffraction électronique a mis en évidence l'existence de tels domaines dans les couches minces de MAPbI$_3$ [1], tous caractérisés par une orientation de l'axe tétragonal c dans le plan (Figure 1.b).

Cette observation est en accord avec les mesures de diffraction des rayons X qui indiquent que, quelle que soit la synthèse utilisée, les couches minces de MAPbI$_3$ sont majoritairement orientées avec l'axe c dans le plan. Des domaines pour lesquels l'axe c est perpendiculaire au plan de la couche peuvent toutefois être observés, dans certaines conditions de contrainte de la perovskite. Nous présenterons ici les résultats d'une étude de ces domaines ferroelastiques par imagerie en diffraction des rayon X effectuée à l'ESRF [2] qui nous a permis d'observer la conversion entre deux types de variants au cours de la mesure.

Dans un second temps, nous proposerons de relier l'observation des différentes orientations de domaines à l'état de contrainte de la couche. Les couches de MAPI sont fréquemment contraintes ; l'une des origines peut en être la différence de coefficient d'expansion thermique (CTE) entre la couche et le substrat. En effet les pérovskites hybrides sont connues pour avoir un CTE élevé, environ un ordre de grandeur plus grand que celui du substrat [3]. Nous montrerons que l'orientation des domaines dans la phase tétragonale dépend des déformations observées du réseau cristallin de MAPI dans la phase cubique.

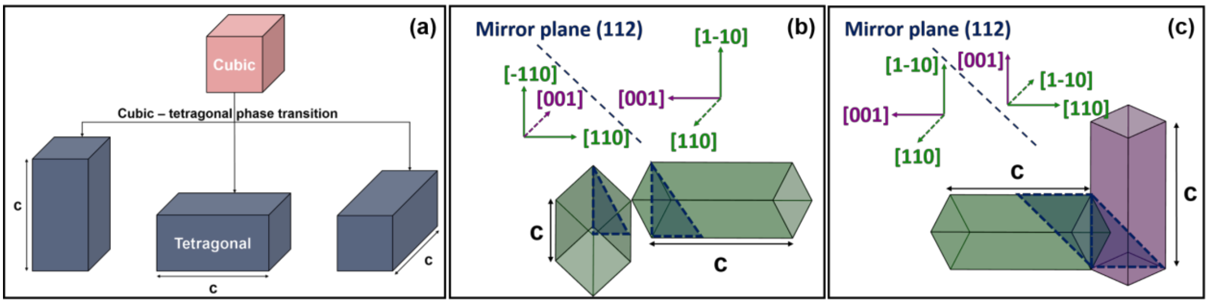

Figure 1(a) Schématisation de la transition de phase cubique-tétragonale, menant à la formation de trois orientations différentes mais équivalentes énergétiquement de l'axe tétragonal c. Macles ferroélastiques identifiées sur les couches minces MAPbI$_3$ par TEM [X] (b) et par notre étude.(c)

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Tetrazine-incorporating layered halide perovskites featuring type II electronic interface: a small cation with several optical and electronic resonances

Ferdinand Lédée [a,b], Pierre Audebert [b], Gaëlle Trippé-Allard [a], Laurent Galmiche [b], Damien Garrot [c], Jérôme Marrot [d], Jean-Sébastien Lauret [a], Emmanuelle Deleporte [a], Claudine Katan [e], Jacky Even [f], Claudio Quarti [e,g]

[a] Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupelec, LuMIn (Laboratoire Lumière, Matière et Interfaces), 91190 Gif-sur-Yvette, France.
[b] Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM (Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires) - UMR 8531, 91190 Gif-sur-Yvette, France.
[c] Université Paris-Saclay, UVSQ, CNRS, GEMaC (Groupe d'étude de la Matière Condensée) – UMR 8635, 78000 Versailles, France.
[d] Université Paris-Saclay, UVSQ, CNRS, ILV (Institut Lavoisier de Versailles) - UMR 8180, 78000 Versailles, France.
[e] Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F 35000 Rennes, France.
[f] Univ Rennes, INSA Rennes, CNRS, Institut FOTON (Fonctions Optiques pour les Technologies de l'Information) - UMR 6082, 35000 Rennes, France.
[g] University of Mons, Laboratory for Chemistry of Novel Materials, B-7000 Mons, Belgium.

Layered halide perovskites are a class of semiconductors easily produced via chemical approaches and showing unique optical and electronic properties. These materials have a natural quantum-well electronic structure, that is, the band-gap of the inorganic frame is embedded into that of the organic spacers,[1] and feature effective light absorption, positive in-plane transport properties, effective narrow linewidth emission and improved stability against their 3D counterpart.[2] On the other hand, confinement of semiconducting properties in an inorganic is not ideal for applications where photogenerated species are required to effectively travel within the optically active component. This is the typical case of photovoltaics, where ineffective out-of-plane charge transport results in depleted performances for layered halide perovskites, as compared to 3D analogues.[3]

In this frame, substituting the (usually) electronic inert organic spacer with organic chromophores featuring extended π-conjugated core can pave the way for layered materials showing improved charge and energy transport properties.[4] Indeed, the band-gap closing due to extended π-electronic conjugation can result in the (de)stabilization of the frontier orbitals of the spacer, compared to those of the inorganic frame, resulting in the formation of a type II heterojunction at the organic/inorganic interface. Here, we discuss the related charge/energy transfer processes on the basis of recently reported PbX_4 (X=Cl,Br) layered perovskite frame incorporating tetrazine derivative as organic spacer.[5] Thanks to the various energy resonances between the inorganic and the organic component, both at the level of the single particle electronic states and at the level of many-body exciton states, this system represents the ideal test case to discuss in the detail charge and energy transfer processes at the type II interface. Furthermore, the incorporation of this novel chromophore as spacer is based on a new design concept, which exploits heterocycles with large fraction of nitrogen, rather than extending the size of carbon-based π-core.[6] Photoluminescence (PL) and Photoluminescence Excitation (PLE) measurements indicate partial energy transfer from the inorganic frame to the organic component. Furthermore, cutting-edge, periodic DFT simulations suggest potential exciton ionization as potential responsible for the suppressed light emission from the perovskite frame.

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Doping crystalline MAPbBr3 hybrid perovskites with high-fluorescence quantum yield CdSe/CdZnS quantum dots: from emissive thin-films to hybrid single-photon sources

Justine Baronnier, Julien Houel, Christophe Dujardin, Florian Kulzer, and Benoît Mahler
Institut Lumière-Matière, CNRS UMR5306, Université de Lyon 1, 69622 Villeurbanne CEDEX, France

We report on a soft-chemistry method that permits to achieve doping of crystalline methylamonium bromide (MAPbBr3) pervoskite thin-films with high fluorescence quantum-yield CdSe/CdZnS core/shell quantum dots (QDs), while retaining their remarkable fluorescence properties.

Our approach produces thin films of 150 nm thickness with CdSe/CdZnS doping content comprised between 0.01 and 1% in volume. The QDs are embedded in the thin film after an inorganic ligand-exchange with halide ions, allowing direct contact between the QDs and the perovskite matrix. Ensemble photoluminescence (PL) measurements demonstrate emission of the QDs after incorporation into the MAPbBr3.

We introduce two types of coupling to describe Photoluminescence excitation (PLE) characterization of the thin films: from MAPbBr3 exciton to QDs, and from QDs to MAPbBr3 shallow defects. We show that the amplitude of these couplings is sample dependent. PL experiments in a confocal geometry demonstrate that high MAPbBr3 exciton-to-QD couplings amplitude are associated to an homogeneous distribution of the QDs in the perovskite matrix, while lower couplings are associated to matrix doped with QD clusters.

We report demonstrate via local PLE experiments on a QD-doped perovskite thin-film, that the coupling amplitudes are spatially dependent.

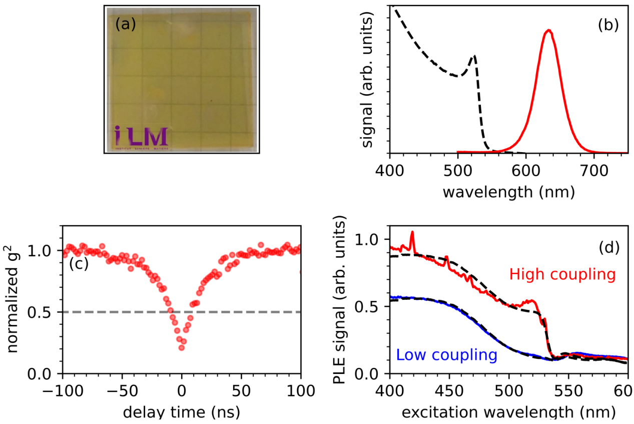

Fig. 1 : (a) 22 x 22 mm^2 MAPBr$_3$ perovskite thin-film doped with CdSe/CdZnS QDs. (b) Absorption of perovskite thin-film (dashed-black) and fluorescence spectrum of QDs (red). (c) Anti-bunching measured on a single QD-in-perovskite hybrid. (d) PLE spectra obtained for two different QD-in-perovskite samples (red and blue) and the corresponding simulated curves (black dashed).

We present fluorescence lifetime imaging microscopy (FLIM) experiments on these systems which reveal an increase of the MAPbBr3 emission lifetime at the QD cluster locations combined with higher emission intensity, leading to the speculation that QDs act as seeds to increase the crystalline quality of the MAPbBr3 matrix around the clusters. We find that that crystallinity enhancement occurs up to 2 µm around the QDs.

Finally, we demonstrate single photon emission from a single QD-in-perovskite hybrid via antibunching measurements and we show that the quantum yield of the inserted QDs is not drastically reduced by detecting up to 800'000 photons/s from a single QD-in-perovskite hybrid.

At high CdSe/CdZnS QD doping level, this work opens the route to hybrid solar concentrator for visible-light harnessing and hybrid-based LEDs, while low-doping content would lead to hybrid single-photon sources embedded in field-effect devices for single charge control to serve as an alternative to solid-state quantum dots.

Doping of the hybrid halide perovskite for the enhanced conductivity

Zuzanna Molenda[1,2], *Sylvain Chambon*[1,3], *Dario Bassani*[2], *Lionel Hirsch*[1]

[1] *Laboratoire de l'Intégration du Matériau au Système, The French National Centre for Scientific Research, Bordeaux, France*
[2] *Institut des Sciences Moléculaires, The French National Centre for Scientific Research, Bordeaux, France*
[3] *Univ. Tokyo CNRS UMI 2820, LIMMS, Tokyo, Japan*

In the age of the global climate crisis caused mainly by the excessive emission of carbonic gases to the atmosphere, the emission-free technologies gain special attention of scientists, industrialists and entrepreneurs. Among others, solar cells seem to be the most promising, as the energy of the sunlight arriving to the Earth is calculated to exceed our current needs by more than 9000 times. Solar cell devices based on hybrid organic-inorganic perovskites, in spite of short time of scientific investigations, proved to achieve the efficiency up to 25.2%[1]. We predict that by doping the perovskite it is possible to increase the open circuit voltage (V_{oc}), which should allow the efficiency to increase by about 30%. We present a simple preparation method of the methylammonium lead iodide based solar cell, where all the layers are deposited by spin-coating. The thickness of the active layer is around 200 nm, while charge selective layers are up to 30 nm thick. The doping of the perovskite active layer was performed by the substitution of Pb-sites with a trivalent transition metal. The preliminary results of X-rays photoelectron spectroscopy (XPS) demonstrated the presence of the dopants in the structure, while the X-rays diffraction (XRD) measurement confirmed the preservation of the perovskite structure. Additionally, the conductivity measurements demonstrated increased lateral and vertical conductivity for the doped material. All these promising results show the necessity to explore perovskite as an active layer of the solar cell devices, as its modification is easily achievable by the uncomplicated means.

[1] National Renewable Energy Laboratory, Best Research-Cell Efficiency Chart, https://www.nrel.gov/pv/cell-efficiency.html (accessed: February 2020)

The effect of MACl on $FA_{1-x}MA_xPbI_3$ perovskite stability

*Fei CHENG, M.N. RAGER Thierry PAUPORTÉ**
Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), UMR8247, and Chimie-Paristech NMR Faciity, 11 rue P. et M. Curie, F-75005 Paris, France

Perovskite solar cell (PSC) has been judged as one of the top ten scientific breakthrough by Science in 2013. In 10 years, single junction PSC got a certified 25.5% power conversion efficiency (PCE). To commercialize PSC, the efficiency and stability are of the same utmost importance. Among all, an effective way to enhance the stability and increase the PCE is the use additives such as ionic liquid, Lewis acid, ammonium salts, halide compounds, into the perovskite precursor solution. Take this a step further, methylammonium chloride (MACl) has shown its excellent performance[1-4]. On the other hand, the main function of MACl is to stabilize the black α-phase of $FAPbI_3$ (FA for formamidinium) which is easily transformed into the yellow photoinactive δ-phase under ambient environment. Our group achieved a best PCE of 22.2% with a MACl dosage of 48%.[3,4] Herein, the different roles of MA^+ and Cl^- in cell stability and precursor stability are presented.

It is commonly known that Cl^- volatilizes during the PVK film annealing and no quantifiable amount of Cl could be detected by EDX in our work. To have a better understanding of the effect of MA^+ on the stability of $FA_{1-x}MA_xPbI_3$ PSC, first, the degradation process of fresh films under ambient conditions was followed by XRD, SEM, NMR. Fig. 1a to Fig. 1d are the corresponding XRD results of stage 1 to 4, the sample pictures have been inserted. Storing the fresh sample (Stage 1, 5% of MA/(FA+MA) by NMR result[4]) in air for 10 days (Avg. humidity 60%, Avg. temperature 19 °C), the δ-phase at 11.8° appeared (stage 2) with black dots left, the transition state is shown in Fig. 1f. Keep storing the sample in air, the intensity of δ-phase peak went stronger than α-phase one at 14 ° (stage 3), the sample turned to yellow. From the results of NMR, the content of MA has decreased to 3.5%. After storing the sample in air for 31 days, PVK turned to δ-phase totally (stage 4), the NMR results showed 3.4% of MA. We concluded that with the $MA_xFA_{1-x}PbI_3$ transition to δ-phase, the concentration of MA decreased, finally, there was still some MA left. Annealing the degraded $FA_{0.97}MA_{0.03}PbI_3$ film for 25 min at 155 °C, transformed the δ-phase to α-phase (Fig. 1i). We then stored the annealed film with a fresh FAMA film in air, and we recorded the degradation process again. From the results in Fig. 1j, after 8 days, the peak intensity of fresh $FA_{0.95}MA_{0.05}PbI_3$ film decreased to its original 24%, while the annealed $FA_{0.97}MA_{0.03}PbI_3$ decreased to 0. To sum up, MA cation plays a vital role in $FAPbI_3$ stability.

To work on the stability effect of Cl^- on precursor, MACl was replaced by MAI. Two bottles of precursor were kept stir in a dry box. From Fig. 1k, the color of MAI precursor is much deeper than the MACl one, which give a glimpse of MACl stabilized the $FA_{1-x}MA_xPbI_3$ precursor.

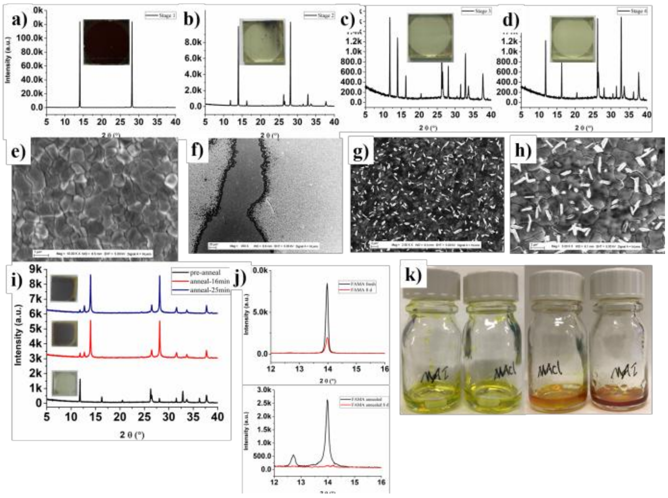

Fig. 1 XRD of a) stage 1, b) stage 2, c) stage 3, d) stage 4; SEM of e) stage 1, f) stage 2, g) stage 3, h) stage 4; i) XRD of annealed $FA_{0.97}MA_{0.03}PbI_3$; j) degradation of fresh and annealed PVK film; k) MAI, MACl precursor aging.

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Session 2

Caractérisations matériaux et modélisation/simulation

Multi-excitons and correlation effects in perovskite nanocrystals

Tan NGUYEN[1]*, Claudine KATAN*[1]*, Jacky EVEN*[2]
[1]*Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France*
[2]*Univ Rennes, INSA Rennes, CNRS, Institut FOTON (Fonctions Optiques pour les Technologies de l'informatiON) - UMR 6082, F-35000 Rennes, France*

Up to date, perovskites have remained to be one of the most fashionable names in the research of photovoltaic materials, achieving an efficiency reaching over 25% without the use of tandem structure [1]. Apart from being excellent materials for solar cells, perovskites have also shown to be an extremely promising candidate for both classical and quantum light sources [2, 3]. Recent advancements in synthesis and surface treatment have allowed a more precise control of emission from nanostructures [4, 5]. In this context, our theoretical work aims to investigate the electronic and optical properties of the systems of single exciton and beyond. Previous calculations on nanocubes or spherical nanocrystals have demonstrated the correlation origin of exciton fine-structure [6] and biexciton/trion emission [7]. In this talk, we will present the configuration interaction approach to take into account the correlation effects in these systems in a more systematic and complete manner.

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Dynamic Temperature Effects in Perovskite Solar Cells and Energy Yield

Pilar Lopez-Varo,[a] Mohamed Amara,[b] Stefania Cacovich,[c] Arthur Julien,[a] Armelle Yaïche,[d] Mohamed Jouhari,[a] Jean Rousset,[d] Philip Schulz,[c] Jean-François Guillemoles,[c] and Jean-Baptiste Puel [a,d]
a. Institut Photovoltaïque d'Île-de-France (IPVF), 18 Boulevard Thomas Gobert, Palaiseau, 91120, France.
b. Université de Lyon, INL-UMR 5270, CNRS, INSA-Lyon, Lyon, 69621, France.
c. CNRS, IPVF, UMR 9006, 18 Boulevard Thomas Gobert, Palaiseau, 91120, France.
d. Électricité de France, EDF, R&D, 18 Boulevard Thomas Gobert, Palaiseau, 91120, France.

Understanding the influence of the temperature on the performance of perovskite solar cells (PSCs) is essential for device optimization and improving the stability of devices in outdoor conditions [1-4]. In addition, knowing the transient thermal response of PSCs (in terms of efficiency and cell temperature) to an external agent change (light intensity, temperature, wind speed) is essential to determine the span of temperature required in the experimental measurement protocols [2,3]. In this work, we study the dynamic temperature-dependent performance of PSCs cell temperature and efficiency) and propose a full model to predict its energy yield (EY) under realistic conditions (See Figure 1). This model stands out for the inclusion of a robust thermal model which allows to estimate the cell temperature from given meteorological conditions. A thermal transient resistor-capacitor (RC) circuit model, previously developed and validated for silicon photovoltaic modules[5], is adapted to estimate the cell temperature and simulate the transient thermal performance of the perovskite solar cell as a function of device parameters and environmental variables. We measure the current-voltage curves as a function of the temperature and light intensities and extract its efficiency which allows the prediction of the device performance. Linking the experimental electrical and optical dependence of PSCs and the thermal model we analyze the most sensible layers that increases the device temperature. Finally, we evaluate the EY of PSC working on different geographical locations and show that the impact of temperature on this prediction can be more than 10 %. The proper calculation of the cell temperature is essential not only to calculate the EY, but also as an input to predict the lifetime of the device [6].

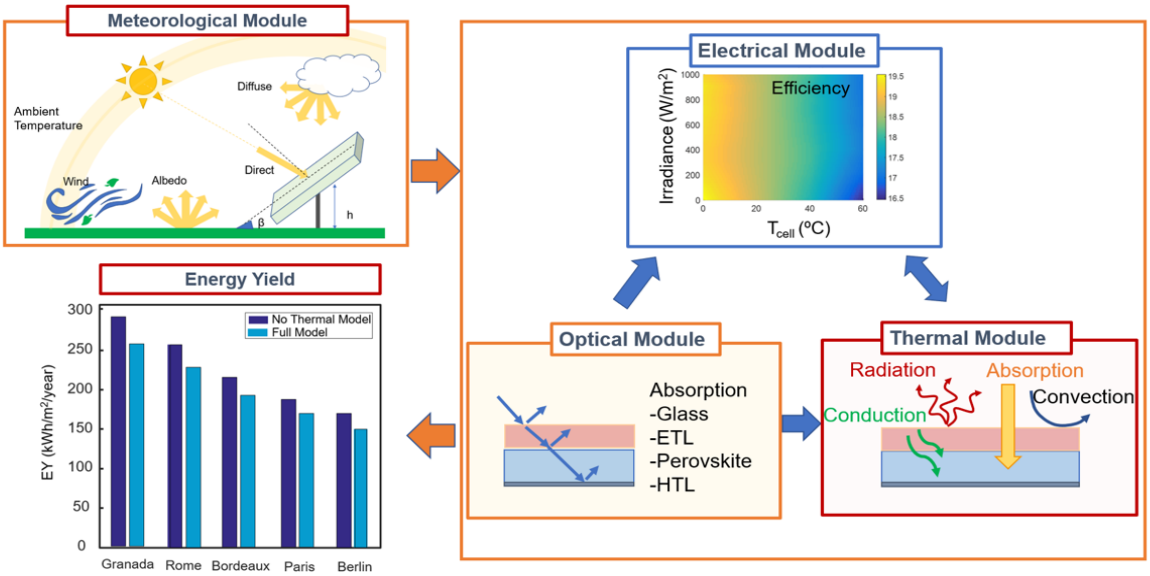

Figure 1. Schematic of the software meteorological, electrical, optical and thermal modules. The output is the annual EY production calculated in different geographical locations under different considerations: (1) experimental constant efficiency at room temperature, and (2) thermal model and the matrix of efficiencies.

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Etude du bruit dans les dispositifs détecteurs à base de monocristaux de $MAPbBr_3$: applications en spectroscopie gamma.

Oriane Baussens[1], *Guillaume Montemont*[1], *Kim Abdoul-Carime*[1], *Lionel Hirsch*[2], *Jean-Marie Verilhac*[3], *Alain Ibanez*[4], *Julien Zaccaro*[4], *Eric Gros D'Aillon*[1]
[1] *Univ. Grenoble Alpes, CEA, LETI, F38000 Grenoble, France*
[2] *Univ.Bordeaux, IMS, CNRS, UMR 5218, Bordeaux INP, ENSCBP, F33405 Talence, France*
[3] *Univ. Grenoble Alpes, CEA, LITEN, F38000 Grenoble, France*
[4] *Univ. Grenoble Alpes, CNRS, Institut Néel, F38042 Grenoble, France*

La spectroscopie gamma est un champ qui recouvre de nombreuses applications telles que la sureté nucléaire, l'imagerie biomédicale et l'instrumentation scientifique. Les semi-conduteurs classiques utilisés en spectroscopie gamma (Ge, CdZnTe…) présentent de très bonnes performances spectrométriques mais ont des limitations liées à leur coût élevé, leur difficulté de fabrication en grande surface et la nécessité d'un refroidissement pour le germanium. Ces limitations pourraient être résolues par l'utilisation de matériaux pérovskites.

Depuis 2016, des études sur les pérovskites ont montrées qu'une résolution en énergie (à 59.5 keV, source ^{241}Am) d'environ 10% de largeur à mi-hauteur pouvait être atteinte avec des monocristaux de $CsPbBr_3$[1] et $MAPbI_3$[2] et de 35% pour des monocristaux de $MAPbBr_{2.85}Cl_{0.15}$[3]. Ces chiffres sont encore trop élevés pour envisager l'utilisation de pérovskites en spectroscopie gamma. Il est donc indispensable d'identifier les facteurs qui limitent la résolution spectrale.

Notre étude a porté sur des dispositifs réalisés à bases de monocristaux (≈ 4×4×1mm^3) de $MAPbBr_3$. Ces monocristaux ont été fabriqués par croissance en solution[4]. Des électrodes en chrome ont ensuite été évaporées sur deux faces opposées préalablement polies.

Grâce à des mesures de comptage de photons gamma, nous avons montré que le niveau de bruit des détecteurs est limitant pour la mesure de photons de basse énergie (<180keV). Ce constat pose la question de l'origine du bruit. Pour répondre à cette question nous avons mesuré la densité spectrale de puissance (dsp) du bruit de ces dispositifs en fonction de la tension de polarisation.

Nous avons pu ainsi montrer que pour des tensions de polarisation nulles, les détecteurs se comportent comme leur schéma électrique équivalent idéal (Figure 1). Dans ce cas, la source de bruit majoritaire est thermique. Par contre, pour des tensions de polarisation non nulles, nous avons montré que le comportement des dispositifs ne dépend pas majoritairement du courant de fuite mais surtout de leur bruit en 1/f (Figure 2).

L'étape suivante consistera, d'une part, à gagner une plus grande compréhension des mécanismes physiques à l'origine du bruit en 1/f, et d'autre part, à étudier le bruit dans des gammes de fréquences plus basses (≈Hz) pour des applications en radiographie X.

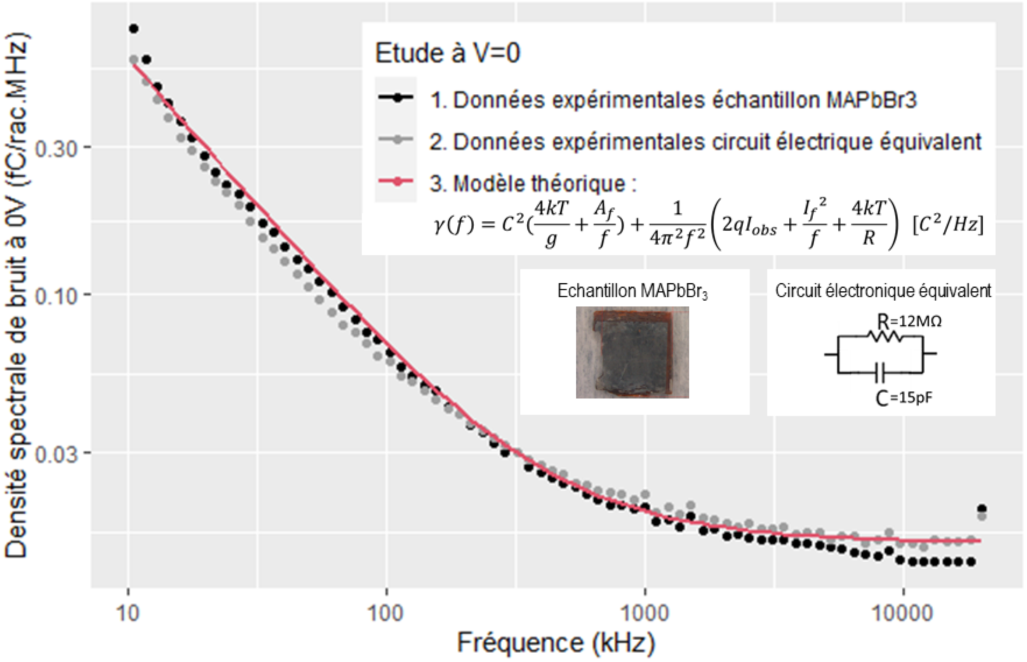

Figure 1 : Comparaison de la dsp de bruit d'un monocristal de MAPbBr$_3$ à polarisation nulle avec la dsp de bruit du montage électrique équivalent et avec le modèle théorique.

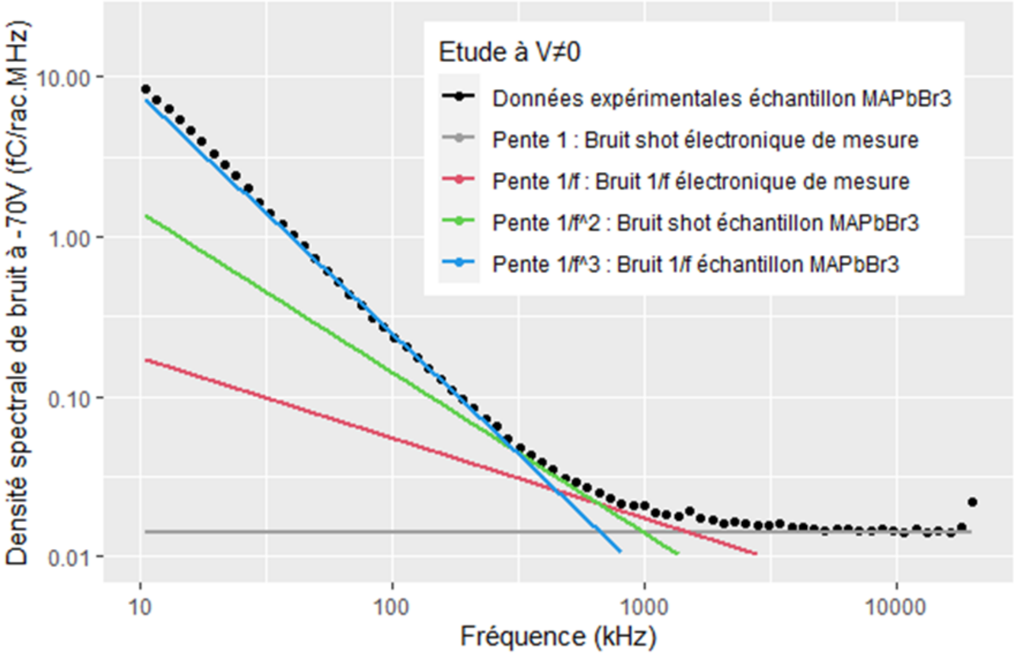

Figure 2 : Etude des composantes fréquentielles de la densité spectrale de bruit d'un monocristal de MAPbBr$_3$ polarisé à -70V.

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Stabilisation de pérovskites halogénées inorganiques par insertion de phase 2D et étude structurale par DRX in-situ

Edouard Breniaux, Pascal Dufour*, Christophe Tenailleau**

**CIRIMAT, Université de Toulouse, CNRS, Toulouse - France*

Inorganic halide perovskite materials research has known an incredible growth over the past decade. A recent record of 18% PCE with $CsPbI_3$ perovskite underpin the expectation for these materials to be a great candidate for solar cells. However, as for the majority of perovskite materials, stability against time and moisture is an issue to be addressed for industrialization.

The use of 2D materials for perovskite phase stabilization has been largely studied in the literature, generally using big organic spacers to induce the separation of large perovskite blocks, which avoid moisture penetration and gives a longer life-time to photovoltaic device. However, the use of organic spacers can increase the bandgap of perovskite active film, and induce thermodynamic barriers that modifies the energetic landscape and that might be detrimental to charge carrier mobility.

Our main focus is the use of the quite recently discovered Ruddlesden Popper structure $Cs_2PbCl_2I_2$ for the stabilization of $CsPbI_xBr_{3-x}$ for an all-inorganic 3D/2D structure. We show the friendly synthesis of such 2D structure by conventional spin-coating route and the photovoltaic properties of the pure phase. This phase is then added to the so-called 3D all-inorganic perovskite solution for spin-coated thin film deposition. In-situ XRD analysis is operated on freshly spin-coated films on ITO substrate. The 3D/2D mix shows an interesting preferential orientation along 14° and 28° in 2-theta XRD peaks that is not observed for pure all-inorganic 3D perovskite. This effect is reproducible and can be observed on different Bromine/Iodine stoichiometry. We meticulously studied stability of such mixture upon heating, and showed that the texture brought by 2D phase allows to stabilize the $CsPbI_3$ black phase at room temperature under nitrogen, while the reference sample shows the reappearance of the undesired yellow non-perovskite structure. The effect of annealing temperature over thin film morphology is observed and the film shows increased compacity and grains size as temperature increases. Such all-inorganic 3D/2D phase is quite new in the literature, and offers a remarkable possibility to stabilize perovskite structure without the use of organic molecules.

Large fluctuations of the inner electrical potential and electronic properties of halide perovskites

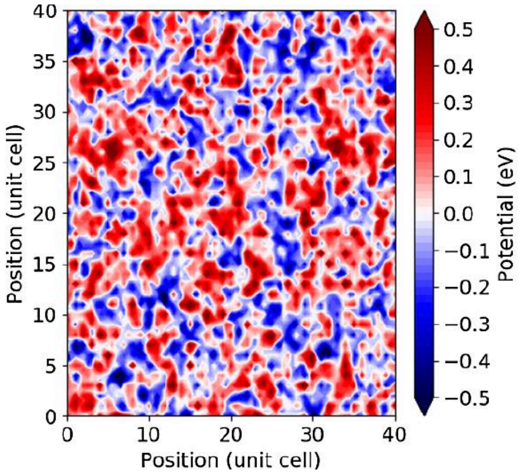
A.Lacroix[1], G.Trambly de Laissardière[2], P. Quémerais[1], J.P. Julien[1] and D. Mayou[1]
1)Université Grenoble Alpes, CNRS, Institut Néel, F-38042 Grenoble, France
2)CY Cergy Paris University CNRS, LPTM, 95302 Cergy-Pontoise, France

In a recent theoretical work [1,2] we analyze the electronic properties of MAPbI3. We use a tight-binding model for electronic structure and an Einstein model for ions vibrations with parameters fitted from ab-initio calculations.

The model is expected to be valid above the Debye temperature. It shows that the thermal displacements of Lead and Iodine ions generate a large electrical potential of about half of the gap (See figure below).

The predicted mobilities of the intrinsic material are of about 80 cm2/Vs at room temperature and the temperature dependences of the mobility and of the gap in the range 200K-350K are in agreement with experimental data.

We show that quantum localization effects, that cannot be described by semi-classical models, are important. When there is additional extrinsic disorder and for mobilities below about 30 cm2/Vs we propose that transport occurs through a non-standard regime. In that case the strong instantaneous disorder localizes the carriers but they can diffuse because their localized state constantly adapts to the motion of the atoms. A similar regime of dynamic disorder has been proposed recently for organic semi-conductors [3].



Instantaneous electrical potential created by ions displacements in MAPbI3. The potential fluctuates on a typical distance which is of a few unit cells. The potential also fluctuates with time due to thermal motion of the ions.

We conclude that polaronic effects are important below the Debye temperature but that above the Debye temperature the large fluctuations of the inner electrical potential play a key role for the electronic mobilities. We suggest that these fluctuations also have a central role for other electrical properties such as electron-hole recombination.

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Conséquences de l'anharmonicité dans les pérovskites halogénés inorganiques : de l'effet Rashba à la ferroélectricité et hyperferroélectricité

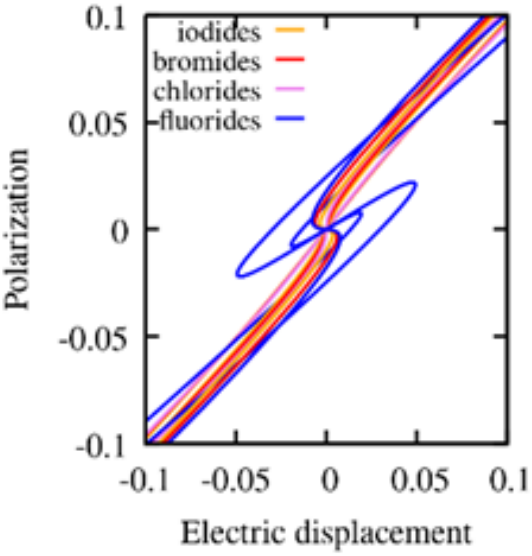
Guido Roma, Service de Recherches de Métallurgie Physique, CEA, Université Paris-Saclay, 91191 Gif sur Yvette, France
Arthur Marronnier, LPICM, CNRS, École Polytechnique, Université Paris-Saclay, F-91128 Palaiseau, France
Jacky Even, Univ Rennes, INSA Rennes, CNRS, Institut FOTON, UMR 6082, F-35000 Rennes, France

La phase pérovskite cubique de $CsPbI_3$ présente un comportement anharmonique qui a été mis en évidence par des calculs du spectre des phonons en théorie de la fonctionnelle de la densité (DFT) [1]. En effet, la structure centro-symétrique présente un phonon mou, qui révèle une brisure de symétrie dont les conséquences sont variées : d'une part, suite à un important effet spin-orbite, un effet Rashba émerge au cours de la dynamique de réseau [2]. D'autre part, puisque le déplacement associé au mode de vibration instable implique un changement de polarisation, on peut soupçonner un comportement ferroélectrique. Nous avons étudié, par des calculs de polarisation en DFT avec la méthode de la phase de Berry, l'équation d'état électrique de $CsPbI_3$ et, plus en général, de pérovskites halogénés $APbX_3$ (A=Cs,Rb,K et X=I, Br, Cl, F) [3] et nous montrons que ces matériaux présentent tous un comportement férroélectrique pour certains d'entre eux, même hyperferroélectrique.

C'est les cas des pérovskites fluorées, en particulier.

Ce comportement sera, dans certains cas, latent en fonction des domaines de stabilité en température des phases pérovskites cubiques.

Ce dernier phénomène, l'hyperferroélectricité, mis en évidence récemment [4], rend la polarisation robuste envers les champs de dépolarisation produit par les charges de surface. Plus en général, ce comportement ferroélectrique sous-jacent pourrait aider à expliquer la dynamique des porteurs dans ces matériaux.



Polarisation en fonction du déplacement diélectrique pour une série de pérovskites halogénées au plomb : l'hystérésis de cette courbe est typique d'un comportement hyperferroélectrique.

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Tailoring exciton-polaritons at room temperature by perovskite-based metasurfaces

Nguyen Ha My Dang[1], Dario Gerace[2], Florian Berry[1], Céline Chevalier[1], Emmanuel Drouard[1], Gaëlle Trippé-Allard[3], Radoslaw Mazurcyk[1], Emmanuelle Deleporte[3], Christian Seassal[1], Hai Son Nguyen[1*]

[1] *Université de Lyon, Institut des Nanotechnologies de Lyon, INL-UMR5270, CNRS, Ecole Centrale de Lyon, 36 avenue Guy de Collongue, Ecully, F-69134, France.*
[2] *Dipartimento di Fisica, Università di Pavia, via Bassi 6, I-27100 Pavia, Italy.*
[3] *Université Paris-Saclay, ENS Paris-Saclay, CNRS, Centrale Supelec, LuMIn, 91405 Orsay, France*

Exciton-polaritons are half-light half-matter excitations arising from the strong coupling regime between cavity photons and excitons of semiconductors [1]. Behaving as superlative non-linear photons thanks to its hybrid nature, exciton-polaritons have been providing a fruitful ground for studying quantum fluid of light and realizing prospective all-optical devices. Here we report on experimental studies of exciton-polaritons at room temperature in resonant metasurfaces made from a sub-wavelength two-dimensional lattice of perovskite pillars. These metasurfaces can be fabricated by either infiltrating perovskite solution into a low refractive index pre-patterned backbone (Fig1a), or thermal imprinting on thin film perovskite with a desire texture mold at high pressure (Fig1b). Room temperature polaritons are demonstrated with a remarkable Rabi splitting in the 200 meV range and moreover, can be engineered to exhibit various characteristics: i) Linear polariton – ideal to study the high-speed polariton propagation (Fig1c); ii) parabolic polariton – suited to study polaritonic non-linear effects (Fig1d); iii) and multivalley polariton – a perfect test bed for parametric scattering study (Fig1e) [2]. In addition, we measured that the propagation of polaritons in these metasurfaces can be up to a hundred micrometers (Fig1f). Impressively, such a macroscopic propagation is backscattering free (Fig1g), confirming its ballistic nature, and also a large-scale homogenity of our polaritonic chip [3]. This ballistic propagation is promising for transmitting information and gating signals between polaritonic devices. Our design is compact, flexible with a wide range of materials and offer high degree of freedom for dispersion engineering. The results suggest a new approach to study exciton-polaritons and pave the way toward large-scale and low-cost integrated polaritonic devices operating at room temperature.

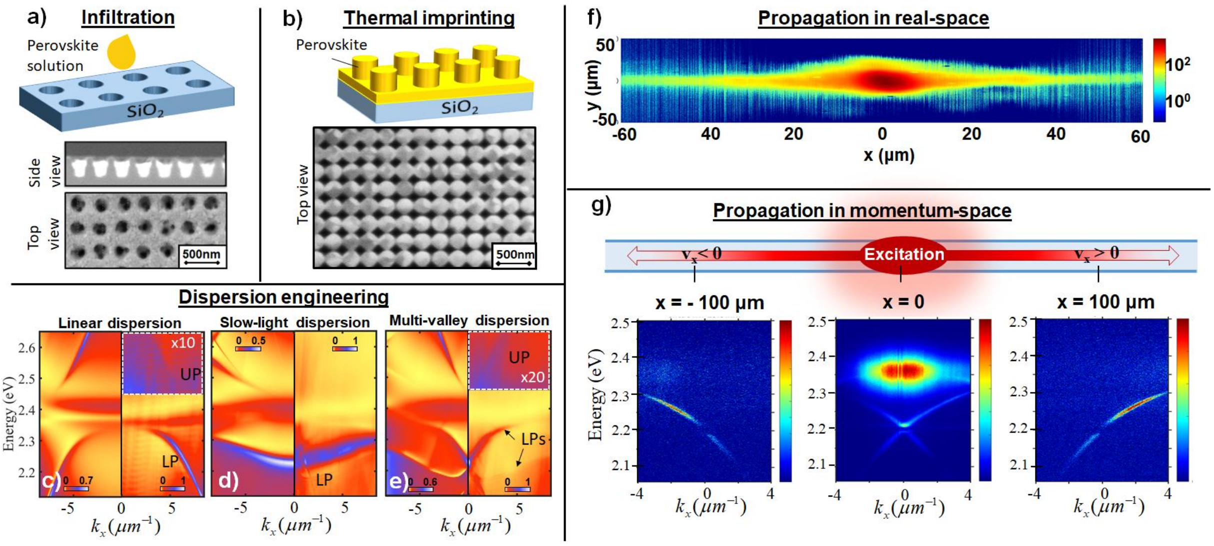

Figure 1. Fabrication scheme with SEM images of fabricated samples corresponding to infiltration method (a) and thermal imprinting method (b). (c,d,e) Angular resolved reflectivity of perovskite-infiltrated-SiO_2 with different lattice parameters obtained by numerical simulation (left panel) and measurement (right panel). (f) Spatially resolved photoluminescence for polariton energy of imprinted perovskite metasurfaces. (g) Angular resolved photoluminescence of imprinted perovskite metasurfaces measured at different propagation position.

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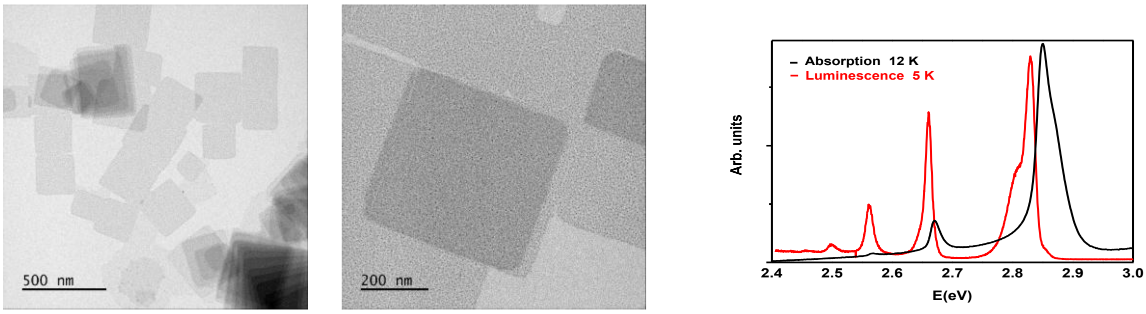
Effets de confinement quantique 1D et 2D dans les nanocristaux de $CsPbBr_3$

Violette Steinmetz, [a] *Julien Ramade,* [a] *Laurent Legrand,* [a] *Thierry Barisien,* [a] *Frédérick Bernardot,* [a] *Emmanuel Lhuillier,* [a] *Mathieu Bernard,* [a] *Maxime Vabre,* [a] *Imen Saïdi,* [b] *Amal Ghribi,* [b] *Kaïs Boujdaria,* [b] *Christophe Testelin* [a] *and Maria Chamarro*

a) *Sorbonne Université, CNRS-UMR 7588, Institut des NanoSciences de Paris, INSP, 4 place Jussieu, F-75005, Paris, France.*
b) *Université de Carthage, Faculté des Sciences de Bizerte, LR01ES15, Laboratoire de Physique des Matériaux : Structure et Propriétés, 7021, Zarzouna Bizerte, Tunisia*

Les nanocristaux colloïdaux de pérovskites inorganiques $CsPbX_3$ (X = Br, Cl, I) font l'objet d'une intense activité de recherche depuis leur première synthèse en 2015, du fait de propriétés optiques exceptionnelles qui permettent d'envisager des nombreuses applications dans des domaines aussi divers que l'opto-électronique, la bio-imagerie ou l'optique quantique.

Le contrôle de la croissance anisotrope des nanocristaux colloïdaux est un enjeu clé dans la génération de matériaux avancés aux fonctionnalités complexes. Dans ce travail, des nanocristaux de $CsPbBr_3$ fortement anisotropes et présentant des raies d'émission et d'absorption très étroites (quelques meV) associées à des effets de confinement selon une ou deux dimensions ont été synthétisés [1]. Parmi ces nanocristaux de forme parallélépipédique, nous distinguons ceux qui nous appelons les « nano-plaquettes, (NPLs) » qui présentent un confinement électronique dans l'épaisseur et des sections rectangulaires d'aire atteignant la fraction de μm^2 (figure 1 (a)) et les « nano-bâtonnets, (NSTs) » qui présentent un confinement à deux dimensions avec des sections transversales de quelques nm^2 et des longueurs de l'ordre de la dizaine de nm (figure 2 (a)). L'analyse conjointe des images de microscopie électronique en transmission (MET) et des spectres d'absorption et de photoluminescence (PL) pris à basse température permet de connecter le type de confinement réellement opérant au niveau électronique à la forme, la taille et l'épaisseur des nanocristaux considérés.



a)

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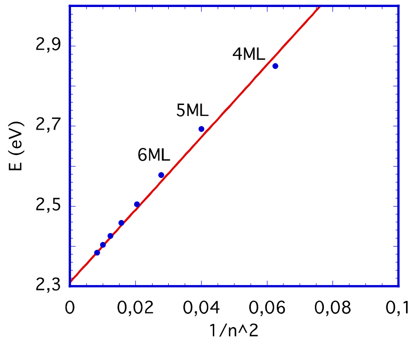


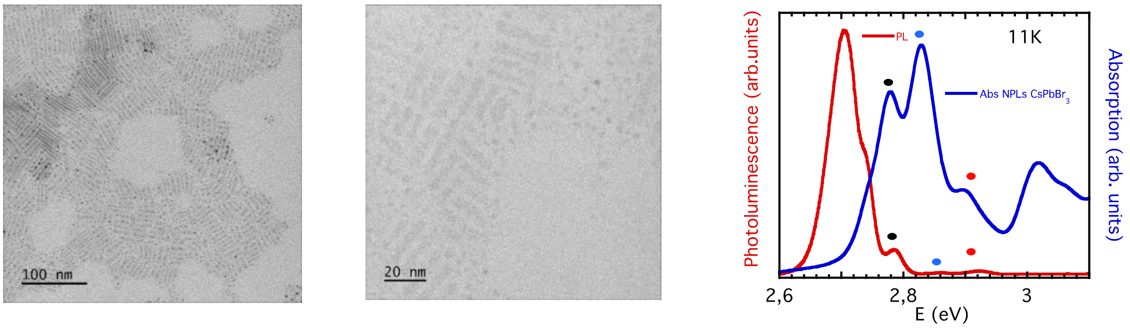
c)

Figure 1(a) Images de microscopie électronique en transmission de films de nanocristaux (synthèse colloïdale modifiée) sous forme de nano-plaquettes étendues aux épaisseurs identifiables grâce à leurs réponses en émission et/ou en absorption.
(b) Spectres d'absorption (en noir) et d'émission (en rouge) aux basses températures.-(c) Les pics d'absorption sont indexés par des entiers n correspondant aux différentes épaisseurs L_z des nano-plaquettes ($L_z = n \times a$ où a est la distance interplanaire de la structure quasi cubique).
NB : L'épaisseur d'une monocouche (ML) est noté a.

Nous montrons, en particulier, que l'énergie des pics d'absorption et de PL *versus* l'inverse du carré de l'épaisseur d’une NPL a un comportement linéaire à partir de 11 monocouches (ML sur la figure 1(c)) soit une épaisseur de 11 × 0.58 = 6,38 nm, jusqu'à 4 monocouches (2,32 nm), comme prévu dans un modèle simple de confinement fort. Conformément aux prédictions théoriques [2], ce résultat montre que, dans ces nanocristaux hautement confinés les effets de confinement diélectrique (dus au contraste diélectrique entre le nanocristal et son environnement) ne jouent pas un rôle déterminant dans l’énergie d’absorption ou d’émission. L'augmentation de l'énergie de liaison de la paire électron - trou qui concoure à abaisser l'énergie de la transition excitonique est compensée par l'augmentation de la "self-énergie" des porteurs.

Dans le cas de nano-bâtonnets, nous montrons que de légères modifications de la morphologie des NSTs conduisent à une modification très drastique de leurs spectres d'absorption. De plus, nous mettons en évidence que l'interaction de l'exciton avec les phonons LO régit l'élargissement des pics d'absorption et de PL à température ambiante et est plus forte que dans les nanocristaux 0D chalchogénures et les NPLs.

À basse température, l’élargissement non homogène est la principale contribution à la largeur de la raie d'absorption dans les NPL et NST. Dans les NPLs très confinés, cette contribution inhomogène ne peut certainement pas résulter de la distribution dans les épaisseurs des NPLs qui conduirait à des décalages énergétiques de l'ordre de la distance inter-pics (≈ 100 meV). Nous pensons que la dispersion de taille latérale est à l'origine de cet élargissement résiduel, compte tenu notamment des plus petits décalages d'énergie de la transition exciton que le confinement induit dans les directions associées~~.~~



a) b)

Figure 2 *(a) Images de microscopie électronique en transmission de films de nanocristaux (synthèse colloïdale modifiée) sous forme de nano-bâtonnets. Dans le panneau de droite les deux dimensions transversales des nano-bâtonnets sont discernables. (b) Spectres d’absorption (bleu) et d’émission (rouge) obtenus à T=11 K dans un film contenant des nano-bâtonnets de taille moyenne 3nm x 4,5 nm X 40nm. Les points colorés identifient les transitions qui se correspondent dans chacun des spectres.*

En conclusion, la croissance maîtrisée de NSTs $CsPbBr_3$ laisse entrevoir des possibilités accrues en direction d'une ingénierie fine des propriétés d'émission. Ce sont des matériaux modèles originaux donnant accès aux effets anisotropes (confinement, forme) sur les propriétés d'exciton des pérovskites halogénures, comme la durée de vie, le couplage aux phonons et la structure fine.

Les NPLs du même matériaux avec quelques monocouches et une très grande surface réalisent de véritables puits quantiques obtenus par voie colloïdale dont les propriétés restent à cerner en particulier en comparaison avec leurs nombreux analogues à base de semiconducteurs III/V ou II/VI. Elles peuvent être post-orientées en utilisant des protocoles d'auto-assemblage interfaciaux et ainsi être intégrées dans des dispositifs optoélectroniques en les combinant avec d'autres matériaux électroniques fonctionnels existants.

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Bright-dark exciton thermal mixing in single CsPbBr$_3$ nanocrystals

M.-R. Amara [a,b], *C. Huo*[a], *C. Diederichs* [b], *Q. Xiong* [a]

[a] *Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore*
[b] *Laboratoire de Physique de l'École Normale Supérieure, ENS, Université PSL, CNRS, Sorbonne Université, Université de Paris, F-75005 Paris, France*

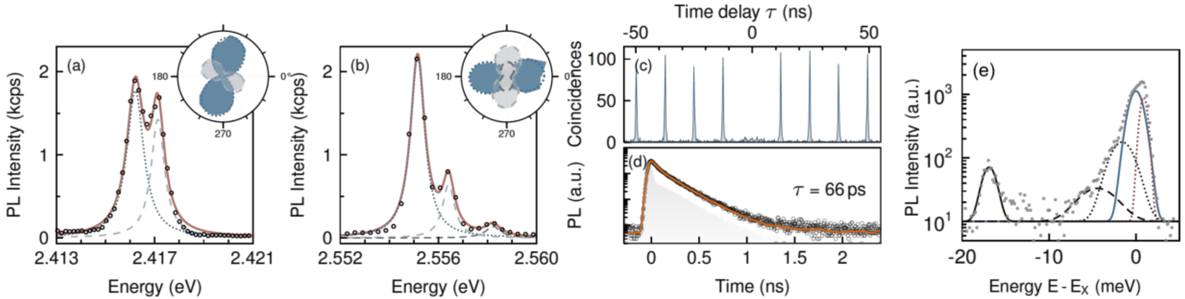
Low-dimensional lead-halide perovskite nanocrystals (pNCs) have emerged in the recent years as new emitters with remarkable optoelectronic properties, all the while being easily synthesized and processed. Recent reports of optical coherence time measurements have further shown that, although new and unprocessed, pNCs readily show favourable characteristics as a quantum light source [1]. The emission nonetheless remains impacted by solid-state decoherent processes such as carrier-phonon scattering and interaction with the electrostatic environment.

Here, we focus on all-inorganic CsPbBr$_3$ NCs in the weak confinement regime ($L \geq 2a_B \sim 7$ nm) dispersed in a polystyrene matrix. They exhibit stable and bright emission at cryogenic temperatures comprised of two- (Fig. 1a) or 3-peak spectra (Fig. 1b) with almost linear polarisation (insets on Fig. 1a,b) attributed to the bright exciton states [2]. The emission arising from this bright exciton manifold shows strong photon antibunching (Fig. 1c) and fast sub-100 ps decay times (Fig. 1d). We use a combination of steady-state photoluminescence (PL) and time-resolved PL to study the emission of individual CsPbBr$_3$ NCs from liquid-helium temperature to ~100 K and gain further understanding of the mechanisms at play, namely exciton-phonon coupling and its interaction with the exciton fine structure in this material.

As previously reported [3], the temperature-dependence of the PL reveals that the emission exhibits a blueshift and a thermal broadening induced mainly by optical phonon scattering. We identify the optical phonon mode at play in the Stokes optical phonon sidebands, together with other lower-energy optical phonon modes that do not seem to play a role in the thermal broadening (Fig. 1e).

Further information is sought from the temperature dependence of the time-resolved PL. While at the lowest temperatures, the emission is fast and mono-exponential, as temperature is increased a longer decay component gains weight and shortens, to become the main decay channel at ~80 K.

This behaviour reveals that the emission results from the interplay between thermally mixed exciton fine structure states (bright and dark). which enables us to estimate the characteristic energies of the phonons involved in this process and rationalize these findings in light of the recent literature on other hybrid and all-inorganic pNCs [5].



Single CsPbBr$_3$ NCs characterisation at liquid helium temperature. *PL spectrum of a single NC with* ***(a)*** *two and* ***(b)*** *three peaks. Insets show the near linear polarisation of each peak.* ***(c)*** *Second-order correlation measurement of the emission arising from this bright manifold revealing strong antibunching.* ***(d)*** *PL decay measurement showing sub-100 ps decay time.* ***(e)*** *PL spectrum revealing optical phonon sidebands redshifted with respect to the lowest bright exciton state (blue).*

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Molecular-level insights into organic-inorganic interfaces in mixed dimensional hybrid perovskites through solid-state NMR spectroscopy

G. N. Manjunatha Reddy
Univ. Lille, CNRS, Centrale Lille Institut, Univ. Artois, UMR 8181-UCCS-Unité de Catalyse et Chimie du Solide, F-59000, France

Abstract

The past five years have seen significant fundamental and technological advancements in the solution-processable semiconductor materials for solar energy conversion. Specifically, hybrid halide perovskites (HPs) are promising light harvesting materials among the emerging photovoltaic technologies today. For example, single-junction solar cells based on HPs have achieved solar-to-electrical energy conversion efficiencies of over 25%, compared to the theoretical Shockley-Queisser limit of 33%. While this trend is expected to continue, the energy harvesting capability of these materials is not withstanding to provide with sustainable large area photovoltaic cells, due to the poor environmental stability and degradation issues. What becomes clear as the field develops is that the compositional engineering of photoactive layers and contact electrodes, and their interfaces, is increasingly important to develop stable and efficient solar cells. In addition, acquiring deep new understandings of structure-stability-property relationships is expected to help in the rational design of solution-processable hybrid perovskite materials for optoelectronics. Here, we present the general application of solid-state NMR (ssNMR) spectroscopy to characterize organic-organic and organic-inorganic interfaces (Figure 1) in mixed dimensional HPs. [1-4] Results on multi-nuclear (^{1}H, ^{13}C, ^{14}N/^{15}N, ^{119}Sn, ^{133}Cs, and ^{207}Pb) ssNMR characterization of 3D perovskites, 2D layered perovskites and "hollow" perovskites will be presented.

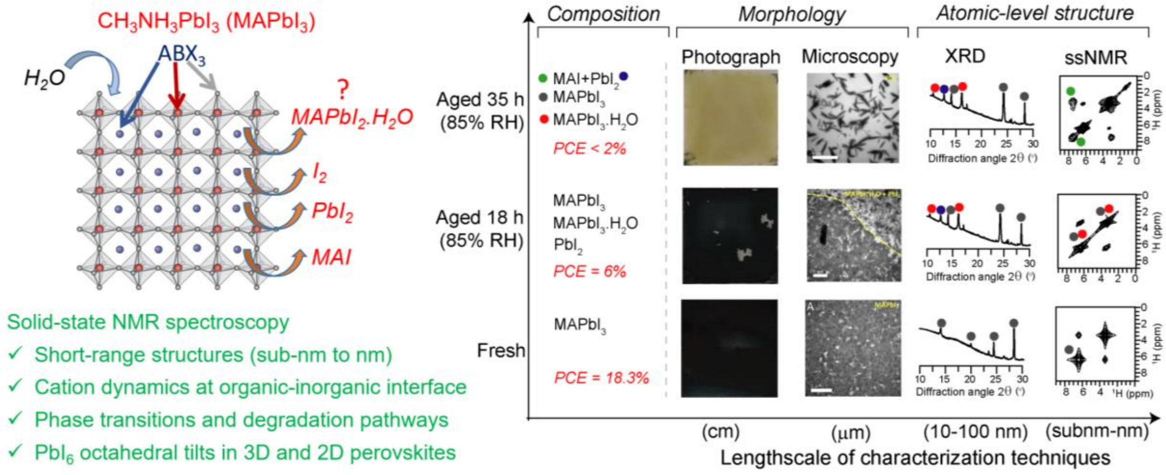

Figure 1. Moisture induced degradation pathway in methylammonium lead iodide perovskite thin films probed at different length scales. ssNMR analysis provides complementary information on the formation of byproducts.

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Resonant Metasurface for Halide Perovskite-Based Emitting Devices: Extraction Efficiency Enhancement and Radiation Pattern on-Demand

Raphaël MERMET – LYAUDOZ[1], Emmanuel DROUARD[1], Céline CHEVALIER[1], Johann BOUCLE[2], Rémi ANTONY[2], Bernard RATIER[2], Pierre COMBEAU[2], Gaëlle TRIPE – ALLARD[3], Emmanuelle DELEPORTE[3], Christian SEASSAL[1], Hai – Son NGUYEN[1]

[1] *Institut des Nanotechnologies de Lyon, INL/CNRS, Université de Lyon, 36 avenue Guy de Collongue, 69130 Ecully, France*

[2] *Institut de Recherche XLIM, CNRS, Université de Limoges, 123 Avenue Albert Thomas, 87000 Limoges*

[3] *Laboratoire LuMIn (Lumières, Matières et Interfaces), Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupélec, 91190 Gif-Sur-Yvette*

Hybrid Organic-Inorganic Perovskites (HOPs), as emerging materials with excellent optical and electrical properties, are prominent candidates for active medium in optoelectronic devices. The popularity of HOPs is often symbolized by its rising in photovoltaic applications [1], with the power conversion efficiency of HOP-based solar cells now exceeds 25%. On the other hand, as direct-bandgap semiconductors, they are now also considered as an alternative to III-V semiconductor for emitting devices such as micro-lasers [2] and Light-Emitting Diode (LED) [3]. Notably, the record of HOP-based LED external efficiency has recently exceeded the 20% milestone.

In this work, we report on the use of resonant metasurfaces to engineer the photoluminescence (PL) emission of HOP thin films. These metasurfaces are sub-wavelength photonic crystals which are obtained by thermal Nano-Imprinting Lithography (NIL) of the HOP thin film (Fig. 1a). We demonstrate experimentally a significant enhancement of the PL of perovskite (Figs. 1e,f). This enhancement is explained by an increase of extraction efficiency thanks to the coupling between HOP emission and Bloch resonances of the metasurface. Moreover, such a coupling also dictates the emission pattern along the energy momentum dispersion of the Bloch resonances that can be tuned through the geometrical parameters of the structure. As a consequence, we can control on-demand the far field emission pattern from quasi-isotropic emission to highly directional one. The structuration of HOP thin film into resonant metasurface by NIL can be implemented in the HOP LED fabrication process flow, providing a versatile mean to enhance the device brightness, and also shaping the emission pattern to match specific applications – like Visible Light Communication (VLC) or usual lightning.

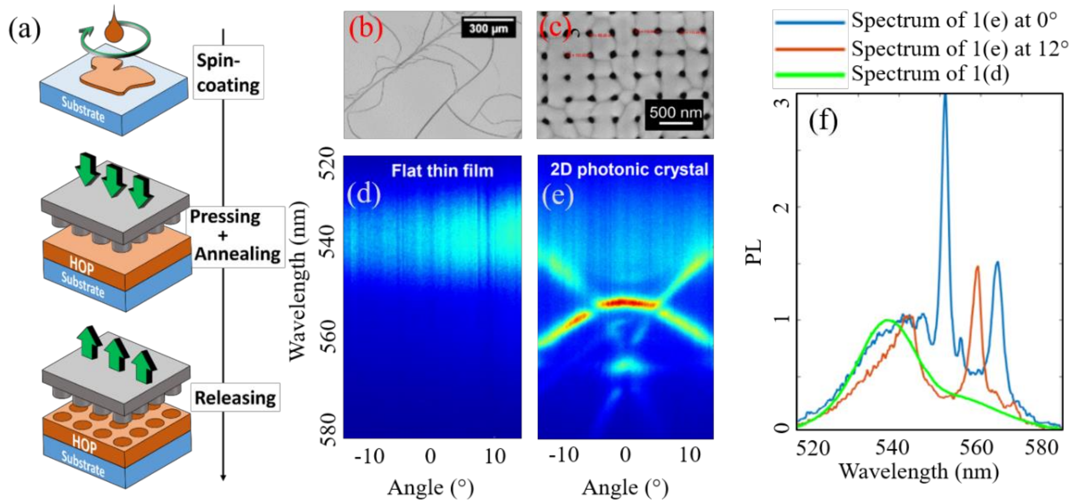

Figure 1: (a) Scheme of the fabrication of HOP metasurface by NIL. **(b)** Microscope image of a flat HOP layer. **(c)** Scanning Electronic Microscopy image of an imprinted HOP layer. **(d,e)** Angle-resolved PL signal of the HOP layer corresponding to (b,c) respectively. **(f)** PL spectra extracted from (d,e).

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Directing random lasing emission using cavity exciton-polaritons

P. Bouteyre,[1] *H. S. Nguyen,*[2] *J.-S. Lauret,*[1] *G. Allard-Trippé,*[1] *G. Delport,*[1] *F. Lédée,*[1]
H. Diab,[1] *A. Belarouci,*[2] *C. Seassal,*[2] *D. Garrot,*[3] *F. Bretenaker,*[1] *and E. Deleporte*[1]*,**

[1]*Université Paris-Saclay, ENS Paris-Saclay, CNRS, Centrale Supélec, LuMIn, Gif-sur-Yvette, France*
[2]*Université de Lyon, Institut des Nanotechnologies de Lyon, INL/CNRS, Ecole Centrale de Lyon, 36 avenue Guy de Collongue, 69130 Ecully, France*
[3]*Université Paris-Saclay, UVSQ, CNRS, GEMaC, 78000, Versailles, France*
**emmanuelle.deleporte@ens-paris-saclay.fr*

Since a couple of years, the halide perovskites $CH_3NH_3PbX_3$, with X a halogen (I, Br, Cl), have emerged in the framework of photovoltaics and of light-emitting devices such as electroluminescent diodes and lasers. These materials can be solution-processed at low temperature and their emission wavelength can be tuned over the entire visible spectrum via chemistry substitutions. In particular, the halide perovskites could address the "green gap" problem in laser sources, i.e. the drop in efficiency of solid-state LEDs and laser diodes emitting green light.

We consider here a one-dimensional planar microcavity containing a large-surface (1 cm^2) spin-coated polycrystalline thin film of the green-emitting $CH_3NH_3PbBr_3$ perovskite, in which the strong coupling regime at room temperature between the photon mode of the Fabry-Perot cavity and the perovskite excitonic mode was previously demonstrated [1]. The exciton-polaritons, which are a linear and coherent superposition of the exciton and photon states, arise from the strong coupling regime.

Random lasing occurs in highly disordered gain media in which cavity feedback is replaced by multiple scattering. The multi-directionality and low coherence of random lasers can satisfy various applications such as speckle-free imaging. However, for typical laser applications, the directionality of the lasing devices is desired.

We demonstrate here a random lasing emission in the green occurring in the microcavity which is directionally filtered by the lower polariton dispersion curve. The angle of emission can be controlled by changing the microcavity detuning. Angles of emission as large as 22° have been experimentally obtained. This result is interesting from a fundamental point of view because it combines two intriguing physical phenomena: the cavity exciton-polariton and the random lasing. Moreover, the control of the random lasing emission direction is a crucial point for optoelectronic applications, such as LIDAR technology.

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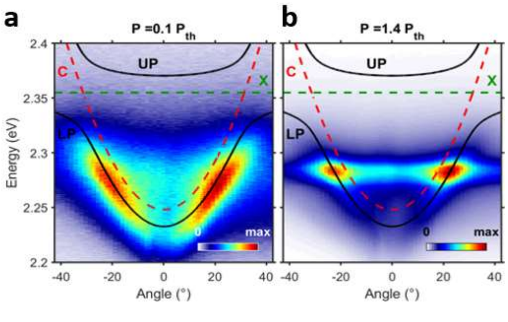

FIG. 1. Angle-resolved photoluminescence (ARPL) pseudo-colour maps a) under and b) above the lasing threshold from one position of the $CH_3NH_3PbBr_3$-based microcavity. The lower and upper cavity polaritons dispersions (black lines), cavity mode dispersions (dashed red line) and the exciton energy (green dashed line) are plotted on top of the ARPL maps.

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Stability of perovskite solar cell's: role of interfaces

PLANES Emilie[1], PERRIN Lara[1], MATHERON Muriel[2], SPALLA Manon[1,2], BERSON Solenn[2] and FLANDIN Lionel[1]

[1]Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble

[2]Univ. Grenoble Alpes, CEA, LITEN, INES, 73375 Le Bourget du Lac, France

Perovskite solar cells represent the most promising concept of solar cells. They combine high efficiency with a strong potential for low cost and good versatility. The main current challenge concerns a lack of stability. The degradation mechanisms of perovskite solar cells have already been studied in details with numerous architectures. It appears that the bulk active layer, the hole and electron transporting layers (HTL and ETL), and each of their interfaces undergo undesirable changes with time. The experimental investigations of the interactions between materials on the stability of a complete device are scarce. The objective of this study is to track the interfaces and the interactions between materials in the stack to reveal the degradation mechanisms. The approach developed relies on the use of partial devices to chase the intrinsic weaknesses of each component, and the possible incompatibility of the interfaces. The current study focuses on the evaluation of the stability of perovskite solar cells, with NIP architectures. Three cases have been selected to show the impact of ETL, HTL and metallic electrode on the degradation of PSCs. The first two studies were performed on a simple perovskite: $MAPbI_{3-x}Cl_x$ monocation formulation, and the devices were submitted in relatively mild ageing conditions (35°C, under dark and inert conditions). In the third case, a multiple anions and cations perovskite was chosen: $FA_{1-x}Cs_xPb(I_{1-y}Br_y)_3$, known for its higher initial performances and improved thermal stability. Consequently, more severe aging conditions have been tested (C1:85°C/0%O_2/0% RH; C2: 85°C/1% O_2/0% RH, C3: 85°C/21% O_2/ 40% RH).

A dominant positron capture and annihilation at vacancies in MAPbI$_3$ and CsMAFAPb(I$_x$Br$_{1-x}$)$_3$ layers on PEDOT-PPS/ITO/glass substrates

P. Aversa[1], M. Kim[2], V. Léger[1], H. Lee[2], D. Tondelier[2], O. Plantevin[3], J. Botsoa[4], P. Desgardin[4], J.E Bourrée[2], L. Liszkay[5], M. Dickmann[6], W. Egger[6], M.F. Barthe[4], B. Geffroy[2,7], C. Corbel[1]*

[1] LSI, CEA/DRF/IRAMIS, CNRS, Ecole polytechnique, Institut Polytechnique de Paris, 91120 Palaiseau, France
[2]LPICM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, 91120, Palaiseau, France
[3]CSNSM, CNRS, Université Paris-Sud, Université Paris-Saclay, 91405 Orsay Campus, France
[4]CEMHTI-UPR3079 CNRS, CS 30058, 3A rue de la Férolerie 45071, Orléans Cedex 2, France
[5]DPhP, CEA/DRF/IRFU, Université Paris-Saclay, 91191 Gif-sur-Yvette Cedex, France
[6]University of Bundeswehr, Werner Heisenberg Weg 39, Munich, Germany
[7]Université Paris-Saclay, CEA, CNRS, NIMBE, LICSEN, 91191, Gif-sur-Yvette, France

**Present Address: C2N (UMR 9001) - Joint research unit CNRS / Université Paris-Saclay, 91120 Palaiseau, France*

Hybrid inorganic-organic halide perovskites attract much attention for their application in optoelectronic devices. However, the performances strongly depend on the quality of the active layers and their capacity to withstand device operation without irreversible damage [1,2]. Light illumination is reported to induce ion migration in HOIPs [3]. Applying a bias in dark in $CH_3NH_3PbI_3$ (MAPbI3) based solar cells also results in ion migration [4]. Dark current measurements give evidence of temperature–dependent charge transport mechanisms in MAPbI$_3$ that are respectively related to electron/hole and ion transport [5]. This questions the existence and/or generation of defects in HOIPs and their role in defect-assisted mechanisms of ion migration under bias and light illumination on photovoltaïc performance.

This work focuses on vacancy-type defects. When in neutral or negatively charged states, such defects capture thermalized positrons in their open volume and give rise to annihilation fingerprints specific to the nature of the vacancy-type defects. Positrons have a most striking reproducible and stable behavior in MAPbI3 and CsMAFAPb(I$_x$Br$_{1-x}$)$_3$ layers spin coated on PEDOT:PPS/ITO/glass substrates in similar conditions by solution growth process. The annihilation characteristics, e-_e+ annihilating pair momentum distribution and positron lifetime spectra, are consistent with huge native vacancy concentration, $\geq 3*10^{18}$cm^{-3}, that efficiently capture thermalized positrons before their annihilation. An additional noticeable property is that the coverage with a PCBM electron transport layer has little effect on these native vacancies. The positron annihilation lifetime in the vacancies, 334(5) ps, has been also earlier observed in sintered MAPbI3 pellets [6]. The nature of the vacancies and their stability with ageing is discussed.

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Observation of internal circuit change of perovskite solar cell according to ageing

Minjin Kim[1], Denis Tondelier[1], Jean-Eric Bourée[1], Yvan Bonnassieux[1], and Bernard Geffroy[1,2]
1. LPICM-CNRS (UMR7647), Ecole Polytechnique, IP Paris, 91128, Palaiseau, France
2. Université Paris-Saclay, CEA, CNRS, NIMBE, LICSEN, 91191 Gif-sur-Yvette, France

Hybrid perovskite has rapidly emerged as a promising candidate for the next generation photovoltaics with power conversion efficiencies (PCEs) up to 25.2%[1]. Compared to commercial silicon-based solar cells, it is price competitive to the simple process and cheap materials[2]. Although these advantages are competitive, the electrical instability as known as hysteresis of the Perovskite Solar Cells PSCs is still an issue. The ion migration that causes this phenomenon still needs research.

We have observed phenomena caused by ion migration within a ITO / PEDOT:PSS / Perovskite / PCBM / Ag structured PSC device in various approaches. Using the GD-OES, mobile ions that move noticeably were identified, and mobile ions and even fixed ions were observed from a relative quantitative point of view[3]. Additionally, we confirmed that ions contribute to electric conduction according to the applied electric field in dark conditions beyond 263K[4].

In this respect we study the influence of ionic distributions in perovskite absorber layers upon ageing time in PSCs. Impedance Spectroscopy (IS) is the tool of choice to investigate material and interface transport properties. In particular, the IS analysis of the medium frequency (MF) and low frequency (LF) region allows to analyse the detailed circuit part[5]. After 3 days ageing in air, these MF and LF regions showed the internal circuit change with additional parallel RC component as seen in Fig.1.

This result shows that the ageing phenomenon modify the distribution of ionic species in the halide perovskite layer, which could influence the charge carrier collection in PSCs.

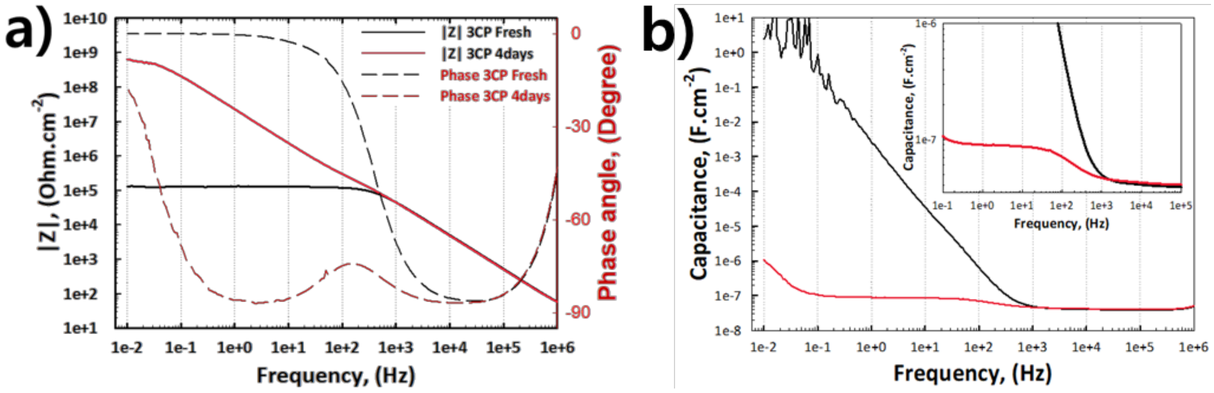

Figure. 1 Summary of IS results a) Bode plot, b) cap. vs Freq. curve comparing fresh PIN device and 4days aged in air and dark condition.

Keywords & Abbreviation: Perovskite Solar Cells (PSCs), ion migration, Impedance Spectroscopy (IS)

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Understanding long-term moisture stability of crystalline and defect passivated methylammonium lead halide perovskites

*Parth Raval[1], Mohammad Ali Akhavan Kazemi[2], Julien Trébosc[1], Frédéric Sauvage[2], Olivier Lafon[1], Laurent Delevoye[1], and G. N. Manjunatha Reddy[1]**

[1]Univ. Lille, CNRS, Centrale Lille Institut, Univ. Artois, UMR 8181−UCCS− Unité de Catalyse et Chimie du Solide, F-59000, Lille, France
[2]Laboratoire de Réactivité et Chimie des Solides (LRCS), UMR CNRS 7314 - Institut de Chimie de Picardie FR 3085, Université de Picardie Jules Verne, 33 rue Saint Leu, FR-80039 Amiens Cedex, France.

Abstract

Hybrid halide perovskites have drawn significant attention due to their outstanding photovoltaic capabilities. However, these materials exhibit poor environmental stability regarding moisture, light, and temperature, limiting the long-term performance in solar cells. Here, we present the multi-technique approach that combines solid-state NMR spectroscopy, X-ray diffraction, and electron microscopy to gain atomic-level insights into the moisture-induced degradation pathways in crystalline 3D methylammonium lead iodide ($MAPbI_3$) perovskites. The influence of moisture (40% and 85% relative humidity) on the $MAPbI_3$ is examined over a year using *ex-situ* ssNMR measurements. In particular, 1D ^{1}H and 2D ^{1}H-^{1}H correlation experiments allow the changes in the local structures of organic cations to be measured and distinguished in fresh and moisture aged materials. These results are further corroborated with X-ray diffraction, in operando liquid cell transmission electron microscopy measurements and analyses. By comparison, defect passivated $MAPbI_3$ by dilute concentrations of tertiary propylamine cation (TPA^+, 2-4mol%) exhibits enhanced moisture stability. As a result, defect passivated perovskite devices with only 2 mol% of TPA^+ achieve power conversion efficiencies over 18.5% and retain more than 85% of their initial performances for over 1500 h under ambient conditions (55±5% RH).[1] This work highlights the importance of atomic-level understanding of chemical degradation pathways and the defect passivation routes to achieve stable and efficient hybrid perovskites for photovoltaic applications.[2]

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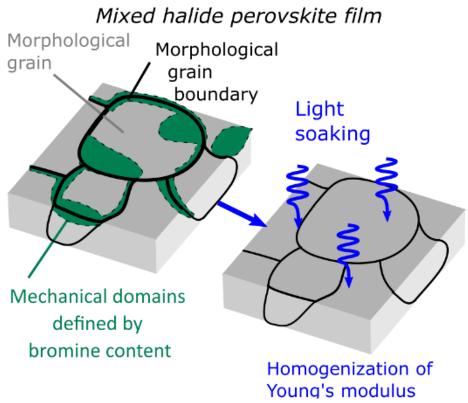
Revealing nanomechanical domains in mixed-halide perovskite films

Ioanna Mela [a] , Chetan Poudel [a] , Miguel Anaya [b] , Géraud Delport ,[b,c] , Kyle Frohna [b], Stuart Macpherson [b] ,
Tiarnan A. S. Doherty [b] , Samuel D. Stranks [a,b] , Clemens F. Kaminski [a]

a Department of Chemical Engineering & Biotechnology, University of Cambridge, Philippa Fawcett Drive,
Cambridge CB3 0AS, UK.
b Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, UK.
c CNRS, UMR 9006, Institut Photovoltaïque d'Ile de France (IPVF), Palaiseau, France

Halide perovskites are a versatile class of semiconductors employed for high performance emerging optoelectronic devices, including flexoelectric systems, yet the influence of their ionic nature on their mechanical behavior is still to be understood. Here, a combination of atomic-force, optical and compositional X-ray microscopy techniques is employed to shed light on the mechanical properties of halide perovskite films at the nanoscale. We reveal mechanical domains within and between morphological grains, enclosed by mechanical boundaries of higher Young's Modulus than the bulk parent material. These mechanical boundaries are associated with the presence of bromide-rich clusters as visualized by nano-X-ray fluorescence mapping. Stiffer regions are specifically and selectively modified upon light soaking the sample, resulting in an overall homogenization of the mechanical properties towards the bulk Young's Modulus. We attribute this behavior to light-induced ion migration processes that homogenize the local chemical distribution, which is accompanied by photobrightening of the photoluminescence within the same region.
https://arxiv.org/abs/2011.08030



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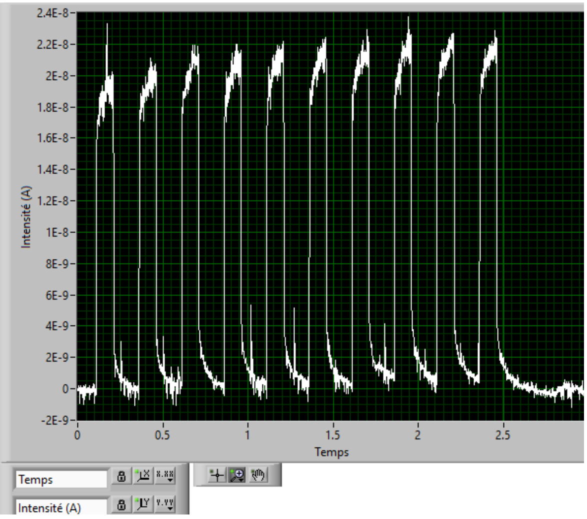
MAPb(Br$_{1-x}$Cl$_x$)$_3$ perovskite materials for direct ionising radiation detection

Javier Alejandro Mayén Guillén − Grenoble Alpes University, CEA LITEN, F38000 Grenoble, France;
Grenoble Alpes University, CNRS, Grenoble INP, Institut Néel, 38042 Grenoble, France
Oriane Baussens - Grenoble Alpes University, CEA LETI, F38000 Grenoble, France
Marian Chapran - Grenoble Alpes University, CEA LETI, F38000 Grenoble, France
Jean-Marie Verilhac − Grenoble Alpes University, CEA LITEN, F38000 Grenoble, France
Eric Gros D'Aillon − Grenoble Alpes University, CEA LETI, F38000 Grenoble, France
Alain Ibanez − Grenoble Alpes University, CNRS, Grenoble INP, Institut Néel, 38042 Grenoble, France
Julien Zaccaro − Grenoble Alpes University, CNRS, Grenoble INP, Institut Néel, 38042 Grenoble, France

Halide based perovskite materials have generated strong and growing attention in the last years for being a hopeful candidate for optoelectronic device applications. Within this perovskite family, organic-inorganic (mixed) halide perovskite materials bring an unprecedented opportunity for radiation detection in direct mode, with their defect tolerance nature, sufficient mobility–lifetime product, and simple crystal growth from solution. Good X-ray absorption is possible thanks to the presence of heavy element such as lead and halogen atoms such as bromine. By definition, single-crystalline halide perovskites exhibit no grain boundaries and possess low trap densities; therefore, they are likely to show superior optoelectronic performances in comparison to their polycrystalline film counterparts [1], [2]. Within our team, methylammonium lead tribromide (MAPbBr$_3$) single crystal (SC) was studied. The crystal growth was optimized [3] and the crystal quality was asserted. Their characterization showed good sensitivity but the response signals showed large dark currents [4]. To improve that critical parameter, using MAPbBr$_3$ as base material, we apply anion engineering within the halide elements: bromine was partially replaced by chlorine We present here mixed halide perovskite SCs via Modified Inverse Temperature Crystallization (MITC) in dimethylformamide (DMF) [3]. Several chlorine contents in solution were studied (y (%) =1, 2, 5, 10). The resulting MAPb(Br$_{1-x}$Cl$_x$)$_3$ crystals were studied by EDX, XRD and photoluminescence (PL) to determine their Cl content (x %), cell parameters (Rietveld refinement) and PL emission. The evolution of these properties was found to be in agreement with the literature [2], [5]. These crystals were used to prepare X-ray detection devices (polishing, electrodes deposition) and the determination of their optoelectronic properties is under way (J-V, response under X-ray radiation) and should help us precise if an optimal composition exist and lift some discrepancies in the literature.

Optical image of resulting SCs: from left to right, MAPbBr$_3$, MAPb(Br$_{0.98}$Cl$_{0.02}$)$_3$, MAPb(Br$_{0.97}$Cl$_{0.03}$)$_3$, MAPb(Br$_{0.94}$Cl$_{0.06}$)$_3$, MAPb(Br$_{0.89}$Cl$_{0.11}$)$_3$ and MAPbCl$_3$



Photocurrent pulses generated in MAPb(Br$_{0.98}$Cl$_{0.02}$)$_3$ by X-rays pulses (sensitivity-voltage)

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Session 3

Dispositifs pérovskites et aspects industriels

Coupled Additives and Interfacial Engineering for High Efficiency and Stable Methylammonium-Free $Cs_{0.1}FA_{0.9}PbI_3$ Perovskite Solar Cells

Daming Zheng, Tao Zhu, Thierry Pauporté
Institut de ChimieParis, CNRS-Chimie ParisTech-PSL Research University, UMR8247, 11rue Pierre et Marie Curie, 75005 Paris, France. E-mail: daming.zheng@chimieparistech.psl.eu

Nowadays, overcoming the stability concerns of perovskite solar cells (PSCs) while keeping high efficiency has become an urgent need for the future of this technology.[1-4] To address this issue, unstable components such as methylammonium must be eliminated, intrinsic outstanding properties of the layers in terms of crystallinity, defect waiving and ionic mobility blocking must be targeted and the film surface must treated for full protection. In this talk, we develop a double engineering approach. First, bimolecular additives, ammonium chloride and potassium chloride, are introduced to assist the formation of $Cs_{0.1}FA_{0.9}PbI_3$ perovskite films and achieve high morphological, structural and optical quality. They are shown to act synergistically to control the crystallization process and passivate structural defects. On the one hand, NH_4Cl allows the control the crystallization growth speed and leads to the formation of large crystal grains with low defect density. On the other hand, KCl favors the PbI_2 precursor solubilization and leads to a purer perovskite phase with reduced defect density. By glow-discharge optical emission spectroscopy (GD-OES), we demonstrate that potassium incorporation in the whole film passivates native defect sites, blocks the ionic mobility and suppresses the J-V curve hysteresis. Secondly, by treating the film surface by propylamine hydroiodide, the formation of a quasi-2D layer is shown. This layer, by passivating surface defects, dramatically suppresses interfacial recombination and boosts the PSC V_{oc} and FF parameters. Finally, we produced optimized PSCs achieving a stable efficiency up to 21.1% and exhibiting a very high stability against heat, light, humidity and electrical external stressors.

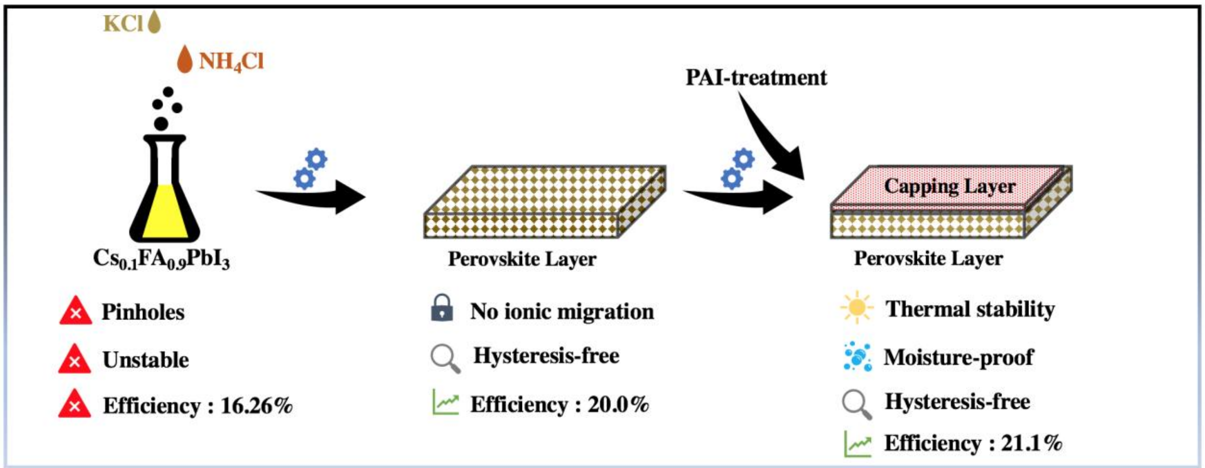

Figure 1. The main preparation steps and their advantages and disadvantages for each stage

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Perovskite solar cells as energy harvesters and data receivers for visible light communications (VLC)

H. Hawashin,[1] *S. Karthick,*[1,2] *B. Ratier,*[1] *T. Trigaud,*[1] *and J. Bouclé,*[1,]*

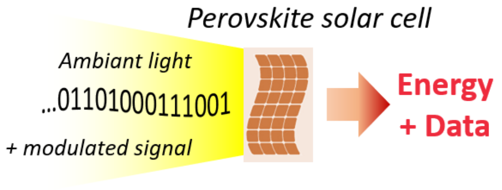
[1] *XLIM UMR 7252, Université de Limoges/CNRS, Faculté des Sciences et Techniques de Limoges, Limoges, France.*
2 CINVESTAV-IPN, Av. Instituto Politécnico Nacional 2508, Col. San Pedro Zacatenco, Ciudad de México, Código Postal 07360, Mexico

** Corresponding authors: johann.boucle@unilim.fr*

The tremendous growth of wireless communications increases significantly the data traffic demand, leading to the congestion of the available radio-frequency bandwidth known as RF spectrum crunch. However, Visible light communications (VLC) are recently proposed as a promising solution for this problem. Recent studies highlight that the VLC can be deployed in a wide domain of applications such as the Internet of things (IoT) or 5G technologies, relying on new VLC innovative concepts for instance: Light Fidelity (LiFi), Body Area Networks (BAN), etc. [1] [2].

Recently, solar cells have been proposed as VLC receivers combining energy harvesting and data receiving simultaneously, which gives the promise for autonomous communication devices [3]. In this context, perovskite solar cells are promising candidates, and triple-cation perovskite solar cells achieved a high data rate of 56 Mbps while demonstrating a simultaneous power conversion efficiency of 18% under indoor illumination conditions [4].

In this work, we focus on the fundamental understanding of the relations between perovskite solar cells performance and their VLC reception capabilities. To this end, perovskite solar cells based on double and triple cations formamidinium lead iodide (mostly $Cs_yFA_{1-y}PbI_{3-x}Br_x$) active layers are processed using Spiro-OMeTAD and SnO_2 as charge extraction layers. The transient response of the devices, probed by impedance spectroscopy, is simulated using adapted equivalent circuits in order to identify the relationships between VLC performance, PV performance, and device architectures. Low and high frequency features are analyzed and discussed, and their impact on device operation are pointed out.



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Enhancing the efficiency and stability of perovskite solar cells by transport layer and interfacial engineering

*Zhelu Hu, Laurent Billot, Hengyang Xiang, Lionel Aigouy, Zhuoying Chen**

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

Organic-inorganic hybrid perovskite solar cells (PSCs) have attracted much attention due to their high power conversion efficiency (>25%) and low-cost fabrication. Yet, improvements are still needed for more stable and higher performing solar cells. In this presentation, two facile routes, respectively focused on the transport layer and the absorber/transport layer interface, are proposed to enhance the photovoltaic efficiency and stability of PSCs: (1) On the first method, a series of TiO_2 nanocolumn electron-transporting photonic structures were intentionally fabricated on half of the compact TiO_2-coated fluorine-doped tin oxide substrate by glancing angle deposition with magnetron sputtering. These vertically aligned nanocolumn arrays were then applied as the electron transport layer into triple-cation lead halide perovskite solar cells based on $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$. (2) On the second method, we investigated the effect of removing the excess PbI_2 at the interface between the triple-cation $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ perovskite and the Spiro-OMETAD hole-transport layer. For this purpose, four different organic salts, including methylammonium iodide (MAI), formamidinium iodide (FAI), methylammonium bromide (MABr) and methylammonium chloride (MACl) were applied and compared.

On the both as-mentioned engineering methods, different characterization methods, including far-field and near-field optical experiments, structural and spectroscopic investigations, impedance spectroscopy, together with solar cell efficiency and in particular device stability measurements are presented together in order to understand the underlying origins of the efficiency and stability enhancement observed in triple-cation perovskite solar cells.

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Functionalization of ETL and HTL metallic oxide by Formamidinium (FA) based Self-Assembled Monolayers for the growth of APbI3 (A= MA, FA) perovskite films

__A. Torkhani__[1, 2], *H.kouki*[1, 2], *F. Mameche*[1], *F. Kouki*[2], *P. Lang*[1]

1: ITODYS University of Paris Diderot, CNRS, 75205 Paris FRANCE

2: LMAPQ Faculty of Sciences of Tunis, University of Tunis El-Manar, 2092 Tunis TUNISIA
torkhaniasma92@gmail.com

Abstract

The performances of hybrid photovoltaic (HPV) devices, particularly Halogenated Perovskite (HP) -based photovoltaic cells, are greatly improved by the insertion of Electron and Hole transport layers (ETL, HTL) metallic oxides MO_x between the conducting electrodes (FTO, metals) and the active layers. The MO_x layer present at electrodes should transport holes and block electrons or the opposite, i.e. blocking holes and transporting electrons.

The control of the interfaces should lead to the improvement of charge collection and the overall device performance.

Their role is to get a better control of MOx surface, notably by the suppressing of interfacial defects and charge trapping. Grafting of adequate functionalized Self-Assembled Monolayers (SAMs) may solve the issue. These monolayers X-P-Y (see picture) aim i) to adjust the electronic levels of the MOx layers with those of the HP one ii) to optimize the growth , the structure and global properties of the active film. We address here the grafting of Formamidinium terminated molecules (NH2NH-(Ph_n)-COOH) (Ph= Phenyl, n=0, 1) on MOX layers such as ZnO (ETL) and NiO (HTL). The organization and orientation of the SAMs have been analyzed by IR spectroscopy (PM-IRRAS). Then we studied and compared the influence of such SAMs on the structure of APbI3 perovskite film (A= MA, FA). HP films are characterized by UV-Vis spectroscopy, XR diffraction and Scanning Electron Microscopy SEM.

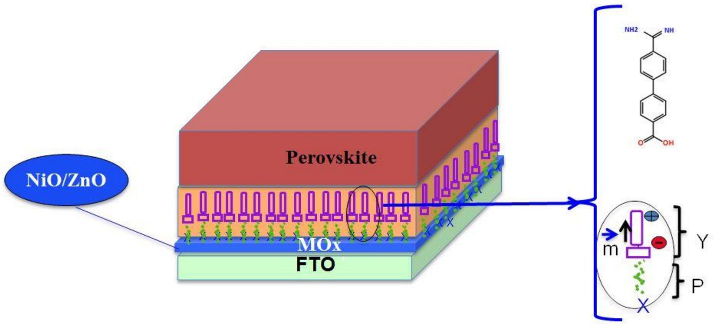

__Fig.1.Layer architecture of perovskite based solar cells.__

Les d-HPs, une nouvelle famille de pérovskites avec une teneur réduite en plomb

Liam Gollino[1]*, Thierry Pauporté*[1]*, Nicolas Mercier*[2]*.*
[1]*Chimie-Paristech, PSL Université, CNRS, Institut de Recherche de Chimie-Paris (IRCP), UMR8247, 11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France*
[2]*Moltech-Anjou, UMR-CNRS 6200, Université d'Angers, 2 Boulevard Lavoisier, 49045 Angers, France*

Les cellules solaires à pérovskites halogénées (PSCs) constituent la technologie la plus récente et prometteuse dans le domaine du photovoltaïque. Ces dispositifs sont actuellement les plus sérieux concurrents des cellules solaires au silicium déjà commercialisées. Cependant, la présence de plomb dans les PSCs entrave fortement leur future commercialisation. Il est donc indispensable, pour la pérennité de cette technologie, de réussir à réduire la teneur en plomb des dispositifs tout en maintenant une efficacité et une stabilité maximales [1,2].

Cette présentation portera sur des PSCs basées sur une nouvelle famille de pérovskite, les d-HPs, pour « deficient-halide perovskites ». Pour fabriquer ces dernières, de gros cations ne respectant pas le facteur de tolérance de Goldschmidt sont insérés au sein de la maille pérovskite. Cette insertion provoque la substitution d'entités PbI^+ (ions Pb^{2+} et I^-) par ces cations et a pour conséquence le maintien de la structure 3D mais avec des lacunes de PbI^+ (cf. Figure 1)[3,4]. Cette famille de composés a une signature spécifique en diffraction des rayons X (DRX).

Nous nous sommes intéressés à trois systèmes: d-MAPI-HEA, d-FAPI-TEA et d-MAPI-IC_2 qui correspondent à des pérovskites $MAPbI_3$ ou $FAPbI_3$ avec une déficience due, respectivement, aux cations hydroxyéthylammonium, thioéthylammonium et au dication iodure d'éthylammonium. Dans un premier temps, nous avons étudié l'effet de la nature des solvants utilisés (DMF, DMSO, NMP, GBL) ainsi que la concentration en précurseurs des solutions sur la qualité des films et des cellules solaires. Nous nous sommes ensuite intéressés à l'étape de dépôt par spin-coating de la pérovskite. Cela a compris : le programme de spin-coating, la nature et le temps d'éjection de l'antisolvant ainsi que la durée et la température de recuit du film pérovskite. Ces études ont permis d'obtenir des films pérovskites de bonnes qualités et d'augmenter significativement les performances de nos dispositifs d-HPs. Ceux-ci délivrent actuellement une efficacité supérieure à 10% mais qui reste bien inférieure à leurs analogues classiques. Les paramètres électriques critiques sont le J_{SC} et le FF. L'insertion de couches d'interfaces a également été testée mais n'a pas été concluante. Des expériences en cours sur le dopage de d-MAPI-HEA par des métaux alcalins semblent quant-à-elles prometteuses et montrent un accroissement de la cristallinité de la pérovskite tout en préservant la signature de la structure d-HPs. Dans le futur, d'autres dopants, d'autres cations, ainsi que divers traitements de surfaces vont être étudiés mais il sera important de s'assurer que ces derniers n'altèrent pas la structure originale des d-HPs.

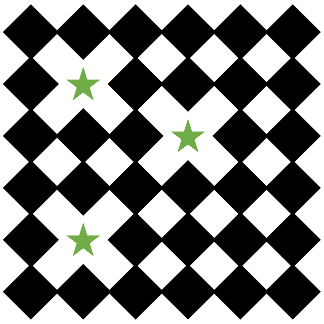

Figure 1: Structure d'une d-HP selon l'axe c. Les étoiles vertes représentent la localisation potentielle du cation inséré au sein de la maille pérovskite

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Study of 2D/3D halide perovskite heterostructure to improve the stability of photovoltaic devices

*T. CAMPOS *[1,2], E. DELEPORTE [1], A. DUCHATELET [2,3], D. GARROT [4], G. TRIPPE-ALLARD [1], J. ROUSSET [2,3]*

*[1] Laboratoire Lumière, Matière et Interfaces (LuMIn), Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupelec, Campus d'Orsay, 91405 Orsay, France * thomas.campos@ens-paris-saclay.fr*
[2] Institut Photovoltaïque d'Ile-de-France (IPVF), 18 Boulevard Thomas Gobert, 91120 Palaiseau, France
[3] EDF R&D, Boulevard Gaspard Monge, 91120 Palaiseau, France
[4] Groupe d'Etudes de la Matière Condensée (GEMAC), Université Versailles Saint-Quentin en Yvelines, CNRS, 45 avenue des Etats-Unis, 78000 Versailles, France

Perovskite based solar cells, using 3D hybrid organic-inorganic halide perovskites as an active layer to absorb sunlight, have recently reached efficiencies over 25% as a single cell (25,5% record since sept. 2020 [1]), getting closer to the silicon technology and the Shockley-Queisser limit. Much attention is paid on perovskites thanks to their interesting properties, making them one of the best candidates for silicon tandem solar cells. However, the perovskite technology is still limited, partly due to the stability of the 3D perovskites towards environmental conditions such as light, heat, and humidity. In parallel, the 2D layered hybrid halide perovskites have drawn an increasing interest by showing higher stability and versatility than their 3D counterparts, but at the expense of efficiency (18,06% record in 2020) [2] due to inferior opto-electronical properties such as transport properties. For this reason, the idea of combining hybrid halide perovskites of 2D and 3D dimensions, in order to create a so-called 2D/3D heterostructure expected to benefit from the high stability of 2D perovskite while maintaining or even increasing the good yield allowed by 3D perovskite, seems to be a promising way to get more stable and efficient silicon-perovskite tandem cells. [3] Two main types of 2D/3D heterostructures are studied in the literature for perovskite solar cells. [4] In the first one called "bulk incorporation", 2D and 3D perovskite phases are mixed in a single layer. The second kind is named "surface coating" and consists in a main bulky layer of 3D perovskite on which a thin layer of 2D perovskite is deposited.

This work aims to develop 2D/3D heterostructures and study their properties, in order to introduce them as the absorbing material in perovskite solar cells. In a first step, we focus our attention on the surface coating 2D/3D structure, using mainly 2D species based on PhenyEthylAmmonium (PEA), one of the most studied and promising ones in the literature. For this purpose, we synthetize a 2D/3D heterostructure based on a triple-cation 3D perovskite, and implement it in solar cells. These cells are characterized by photovoltaic I-V measurements to look over their performances in term of devices. In parallel, several characterisation methods are used in order to get more knowledge on this structure: UV-Visible absorption and Photoluminescence measurements to analyse the optical properties of the material, surface and cross-section SEM, combined with AFM to know the topology and layout of the different layers in the device, XRD to analyse the structural and properties of the material.

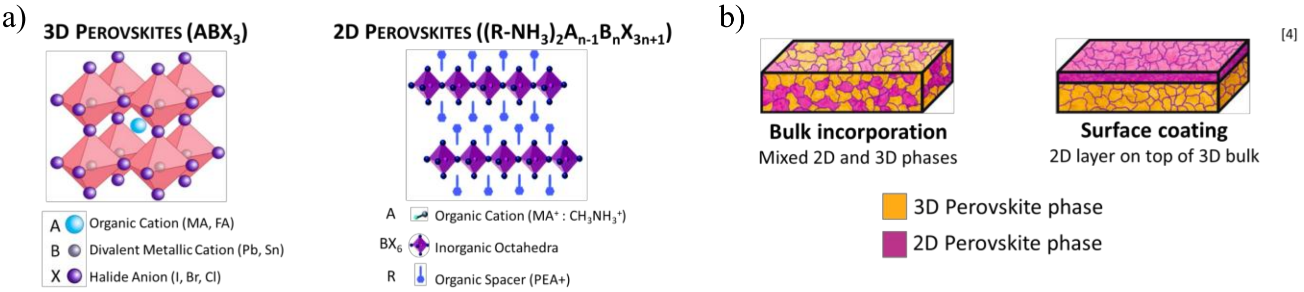

Figure 1: a) 3D and 2D hybrid organic-inorganic halide perovskite structure b) Representation of bulk incorporation and surface coating 2D/3D heterostructure

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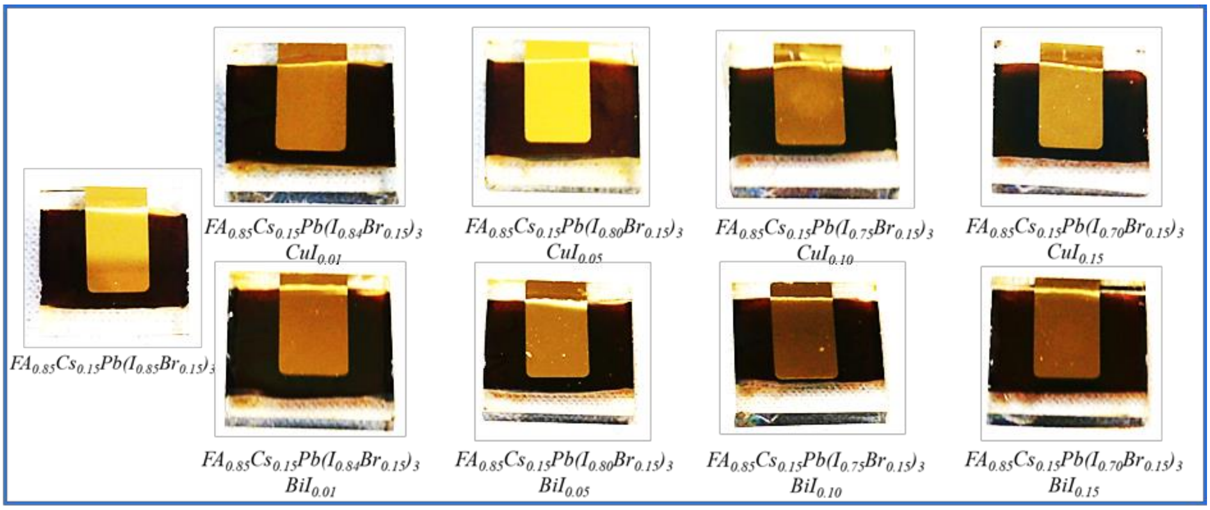
Effect of Copper and Bismuth iodide incorporation in FA-Cs perovskite solar cells by one-step solution process.

S. Karthick[a,b], S. Velumani[a,], J. Bouclé[b,*]*
(a) Programa de Nanociencias y Nanotecnología, Centro de Investigación y de Estudios Avanzados del Instituto Politécnica Nacional (CINVESTAV-IPN), Av. Instituto Politécnico Nacional 2508, Col. San Pedro Zacatenco, Ciudad de México, México, Código Postal 07360.
(b) Univ. Limoges, CNRS, XLIM, UMR 7252, F-87000 Limoges, France.

In recent days, wide bandgap planar mixed cation $FA_{0.85}Cs_{0.15}Pb(I_{0.85}Br_{0.15})_3$ perovskite solar cells showing unimaginable improvements, which is an encouraging candidate in the photovoltaic (PV) field [1-4]. Several approaches are currently proposed to avoid or reduce the lead (Pb) content in the perovskite composition due to its toxicity but also to improve the device stability in ambient conditions. In this context, we systematically investigate the effect of Copper iodide (CuI) and Bisumth iodide (BiI_3) partial incorporation into the double cation perovskite precursor solutions, in an attempt to form $FA_{0.85}Cs_{0.15}Pb(I_{1-X}Br_{0.15})CuI_X$ and $FA_{0.85}Cs_{0.15}Pb(I_{1-X}Br_{0.15})BiI_{3X}$ (where X= 0, 0.01, 0.05, 0.10, 0.15) compounds. We carried out structural, morphological, topographical, and optical studies on these doped perovskite layers in order to emphasize the impact of doping with regard to the undoped reference. Then, the pure planar double cation and Cu- or Bi-doped perovskite solar cells were fabricated and tested. While both CuI or BiI_3 doped perovskite devices demonstrate significantly reduced performance compared to the undoped device. We point out the crucial role of dopants on the active layer morphology and structure in relation with faster recombination kinetics probed by transient photovoltage measurements. Preliminary stability tests under ambient conditions of un-encapsulated devices are also conducted and discussed.

Keywords: formamidinium perovskite solar cells, Copper iodide, Bismuth iodide.



$FA_{0.85}Cs_{0.15}Pb(I_{0.85}Br_{0.15})_3$

$FA_{0.85}Cs_{0.15}Pb(I_{0.84}Br_{0.15})_3$ $CuI_{0.01}$

$FA_{0.85}Cs_{0.15}Pb(I_{0.80}Br_{0.15})_3$ $CuI_{0.05}$

$FA_{0.85}Cs_{0.15}Pb(I_{0.75}Br_{0.15})_3$ $CuI_{0.10}$

$FA_{0.85}Cs_{0.15}Pb(I_{0.70}Br_{0.15})_3$ $CuI_{0.15}$

$FA_{0.85}Cs_{0.15}Pb(I_{0.84}Br_{0.15})_3$ $BiI_{0.01}$

$FA_{0.85}Cs_{0.15}Pb(I_{0.80}Br_{0.15})_3$ $BiI_{0.05}$

$FA_{0.85}Cs_{0.15}Pb(I_{0.75}Br_{0.15})_3$ $BiI_{0.10}$

$FA_{0.85}Cs_{0.15}Pb(I_{0.70}Br_{0.15})_3$ $BiI_{0.15}$

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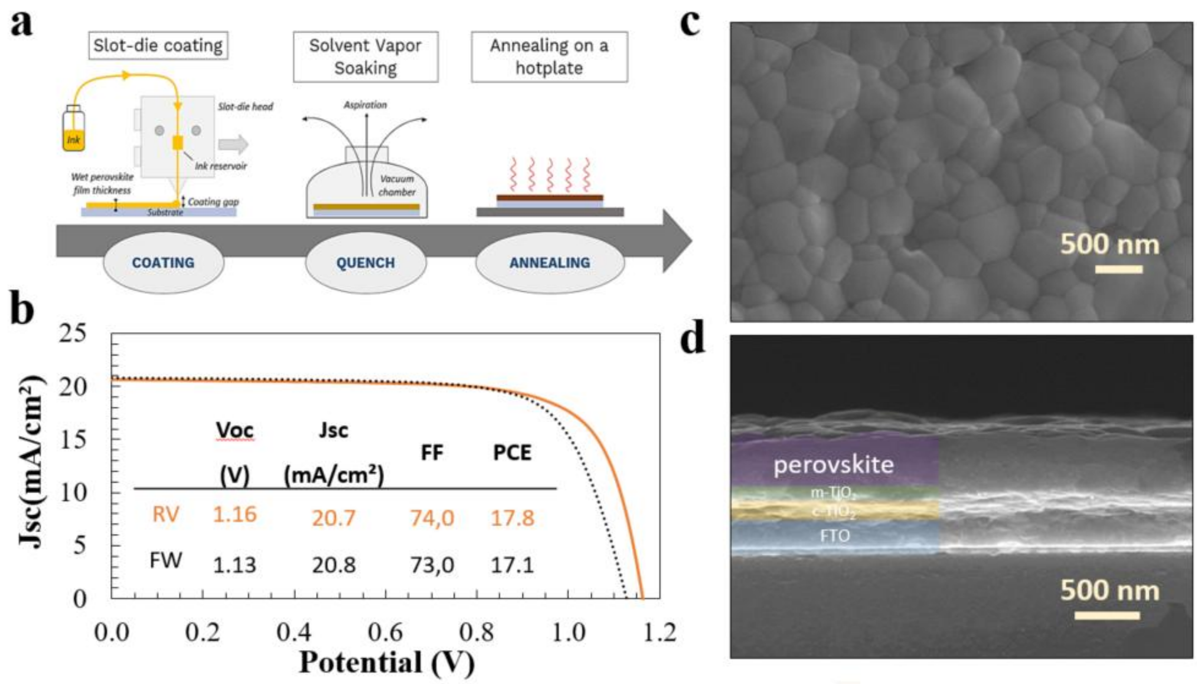
Study of The Synergetic Effects Of Chloride and Surfactants Additions on Perovskite Crystallisation, in A Slot-Die Coating Process for Large-Scale Fabrication

BERNARD Sophie[1,2], MEJAOURI Salim[1,3], CACOVICH Stefania[2], ZIMMERMAN Iwan[2], YAICHE Armelle[1], GBEGNON Stéphanie[2], DUCHATELET Aurélien[1], JUTTEAU Sébastien[1], SAUVAGE Frédéric[3], ROUSSET Jean[1,2].

1 EDF R&D, EDF Lab, Boulevard Gaspard Monge, 91120 Palaiseau, France
2 LRCS, Laboratoire de réactivité et Chimie du Solide (CNRS UMR 7314), Université de Picardie Jules Verne, Hub de l'énergie, 15 Rue Baudelocque, 80039 Amiens, France
3 C2N, Centre de Nanosciences et Nanotechnologies (CNRS UMR 9001), 10 Boulevard Thomas Gobert, 91120 Palaiseau, France
4 IPVF, Institut Photovoltaïque d'Ile de de France (CNRS UMR 9006), 18 boulevard Thomas Gobert - 91120, Palaiseau, France

For the past ten years, perovskite solar cells have known a tremendous development among photovoltaic technologies, rapidly increasing from 3,8% [1] to 25.5% [2] power conversion efficiency (PCE). However, before transferring this technology to commercial applications, one of the main challenges to overcome is the fabrication of high quality perovskite absorber films on large surfaces. Various alternatives to spin-coating have been explored in the literature such as blade coating [3], inkjet coating [4], roll-to-roll [5] or spray coating [6]. But, slot-die coating is one of the most promising techniques. It is easily compatible with high rate fabrication technique like roll-to-roll and allows a sharp control over the uniformity on large surfaces.



	Voc (V)	Jsc (mA/cm²)	FF	PCE
RV	1.16	20.7	74,0	17.8
FW	1.13	20.8	73,0	17.1

Figure 1 : a. Slot-die deposition process, b. I-V curves of the record, cell c. Top-view SEM images of the perovskite layer deposited by slot-die and d. Cross-section SEM image of the perovskite film deposited on Glass/FTO/c-TiO2/m-TiO2

In this work, we emphasis on the influence of the drying method upon the absorber properties. After the slot-die coating deposition, we chose to use a vacuum quench method, which allow a uniform extraction of the solvent, few minutes before annealing *(Fig.a.).* The change of the quench system, from anti-solvent to vacuum aspiration, modify the speed with which the solvent is extracted. Then, it is possible to influence the crystallization mechanisms to fit the new drying environment by changing the perovskite ink composition. We herein propose a method to fabricate a double-cation CsFA perovskite with a double-additives protocol, combining a surfactant and chloride addition through MACl.

A particular difficult challenge is to isolate the action of the surfactant and the chloride during crystallization. We combined PL and morphological characterisations, under different annealing and quench conditions, in order to successfully bring their respective effects out. For example, including MACl into precursor solutions seem to increase the film coverage and grain sizes during secondary grain growth, generating a smooth and pinhole-free perovskite layer with large grain size while surfactant enhance film uniformity and passivate surface defects. We reached over 17.8% PCE on small-scale cells (0.09 cm^2 aperture) *(Fig.1.b)* with optimized ratio of chloride and surfactant, thermal annealing and vacuum conditions.

This approach offers a better understanding of perovskite growth under large-scale fabrication conditions and is an important step towards industrial perovskite devices.

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PEAI-Treatment for High-Efficiency and Stable Solar Cells Based on a MACl-Mediated Grown $FA_{0.94}MA_{0.06}PbI_3$ Perovskite

Tao Zhu,[a] *Daming Zheng,* [a] *Marie-Noelle Rager,* [a] *Jiawen Liu,* [b] *Laurent Coolen*[b] *and Thierry Pauporté**[a]

[a]*Institut de Recherche de Chimie Paris (IRCP), UMR8247, Chimie ParisTech, PSL University, CNRS, France.*
**thierry.pauporte@chimie-paristech.fr ; www.pauportegroup.com*
[b]*Sorbonne Université, CNRS, Institut de NanoSciences de Paris, INSP, F-75005 Paris, France*

Nowadays, complex chemistry and precursor solution compositions are developed to stabilize hybrid perovskite films and boost the efficiency of perovskite solar cells (PSCs).[1-4] In this context, determining the actual composition of these layers, especially in organic cations, and understanding the chemistry behind is challenging. In this presentation, the introduction of methylammonium (MA^+) in formamidinium lead iodide ($FAPbI_3$) 3D perovskite is considered to stabilize the α-phase, whose quantity must be minimized to reduce the material hydrophilicity and its possible destabilization by degassing.[1] The key effects of methylammonium chloride (MACl) additive on the growth of $FA_{1-x}MA_xPbI_3$ perovskite layers are studied. Liquid nuclear magnetic resonance (NMR) is used to analyze the photovoltaic layers. NMR peaks and their origin are identified. The MA and FA content in films actually used in PSCs is reliably measured and prepared over a large additive molar concentration ratio. x is quantified at 0.06±0.01 for pure films, which corresponds to the best entropic compound stabilization.

For further improvement, the treatment of the perovskite surface by a 2-phenylethylammonium iodide (PEAI) solution has been performed.[2] This treatment, without any thermal annealing, leads notably to the spontaneous formation of a crystallized $(PEA)_2PbI_4$ two-dimensional (2D) perovskite nanolayer at the film surface due to partial organic cation dissolution. This buffer layer is shown to favor a fast transfer of the holes toward the hole transporting layer (HTL) and to reduce the recombinations at and near the perovskite/HTL interface in perovskite solar cells (PSCs). It is shown to boost their maximum power conversion efficiency (PCE) from 20.37 to 22.18%, while the hysteresis becomes negligible. It results in PSCs with a stabilized power conversion efficiency as high as 22.1%. These PSCs are shown to be highly stable under solar irradiation, electrical stresses, and high moisture.

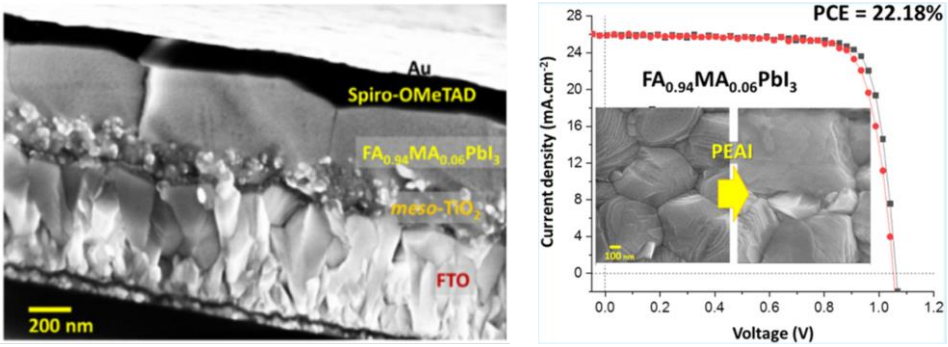

Figure 1. Cross-sectional SEM view of Optimized PSC (left); J-V curves of the champion device (right) and perovskite SEM top view before and after PEAI treatment (right inset).

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Introduction de brome dans des cellules solaires triples mésoscopiques à électrode de carbone

Hindia Nahdi[1,2], Frédéric Oswald[3], Bernard Geffroy[2,3], Denis Tondelier[2], Yvan Bonnassieux[2], Madjid Haddad[1]*

[1]SEGULA Technologies, 19 Rue d'Arras, 92000 Nanterre, France
[2]LPICM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, route de Saclay, 91128 Palaiseau, France
[3]Université Paris-Saclay, CEA, CNRS, NIMBE, LICSEN, 91191, Gif-sur-Yvette, France
**hindia.nahdi@polytechnique.edu*

Les pérovskites hybrides halogénées (ABX$_3$) sont de plus en plus étudiées comme couches absorbantes pour de nouvelles cellules solaires à haute efficacité et bas coût. Elles ont connu le développement le plus rapide jamais enregistré avec des efficacités passées de 3,8% en 2009 à 25,2% en 2019 pour les cellules simples et 29.1% [1] pour les cellules en architecture tandem sur silicium. Un des freins à une utilisation industrielle de ce matériau est leur instabilité, en particulier vis-à-vis de l'eau ce qui les destine plutôt à des applications en intérieur.

Grancini et al. [2] ont réalisé un dispositif pérovskite dont la stabilité a été éprouvée sur plus d'une année. Cette prouesse repose sur une architecture originale à électrode de graphite (figure 1a) et une jonction pérovskite 2D/3D (HO$_2$C(CH$_2$)$_4$NH$_3$)$_2$PbI$_4$/CH$_3$NH$_3$PbI$_3$ (figure 1b) permettant l'utilisation d'un matériau alliant la stabilité des pérovskites 2D et les propriétés opto-électroniques des pérovskites 3D.

Nous présentons ici une l'étude du comportement de cette structure lorsque l'on incorpore du brome dans la composition de la pérovskite. Ces préparations ont été caractérisées par microscopie électronique à balayage couplé à une analyse dispersive en énergie (EDX), diffraction aux rayons X et spectroscopie raman.

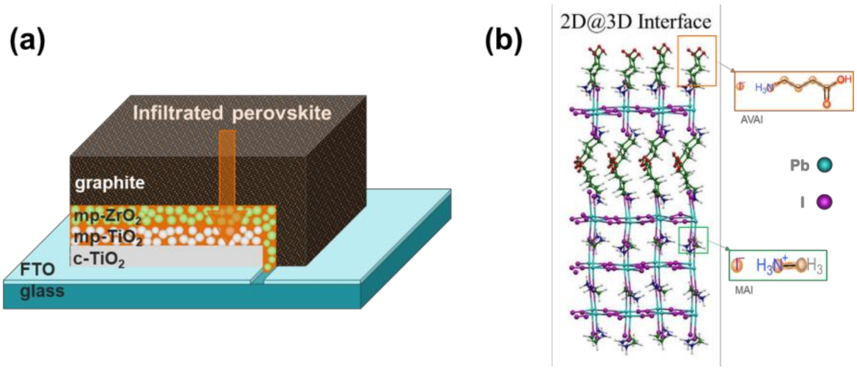

Figure 1. (a) structure de la cellule et (b) modélisation de l'interface 2D/3D. mp = mésoporeux, c = compact

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Control of stability of Perovskite solar cell by Functionalization of intermediate metal oxide layers with tailored Self-Assembled Monolayers in ambient air

Hedi Kouki[1,2], *Asma Torkhani*[1,2], *Faiza Mamèche*[1,2], *Fayçal Kouki*[2], *Philippe Lang*[1]

1:ITODYS, UMR 7086 CNRS, Université de Paris 75013 Paris
2 : LMPQ Faculté des sciences de Tunis, Université Tunis El-Manar, 2092 Tunis, Tunisia
**Koukimedhedi02@gmail.com, *lang@univ- parisdiderot.fr*

Abstract:

The insertion of Electron and Hole transport layers (ETL, HTL) metallic oxides between the conducting electrodes (FTO, metals) and the halide perovskite (HP) film are required in order to transport electrons and block holes or the opposite, i.e. blocking holes and transporting electrons respectively. However these MOx layers may have defects, surface states which limit the reproducibility and cell performances by favorizing the charge recombination. An elegant way to solve this issue consists to modify the MOx layers by adequate functionalized Self-Assembled Monolayers (SAMs). SAM treatment is a convenient way to tailor the work function of the MOx interlayers and to control the growth, structure and stability of HP films. In this context, we address the deposition of various self-assembled monolayers based on bi-functionalized molecules $[(COOH\text{-}(CH_2)_n\text{-}\Phi\text{-}\Phi\text{-}CH_2)_m\text{-}Y)$ ($n, m=0,1$; $Y=CN, NH_2, NH_3^+Cl^-$] on ZnO, WO3 and NiO layers. The organization and orientation of the SAMs have been analyzed by IR spectroscopy (PM-IRRAS). Then we study and compare the influence of such SAMs on the structure and stability of MAPbI3 perovskite film in ambient air and in room temperature. After that, we have integrated those treated films in solar cells architecture. In this work we have proved the benefic effect of the SAM's on photovoltaic parameters.