

JPH 2023

Journées des Pérovskites Halogénées

Livret des résumés
/ Book of abstracts



du Mercredi 31 Mai au Vendredi 2 Juin 2023



Biarritz (France)





Résumés des oraux (dans l'ordre du programme)
/ Oral abstracts (as per the program)



Liste des 22 oraux (dans l'ordre du programme)

/ List of the 22 orals (as per the program)

- 01.** “Perovskite-based NIR photodetectors”
Loïc PAILLARDET – CEA Liten & STMicroelectronics
- 02.** “Redox-active substitutional doping of metal halide perovskites”
Zuzanna MOLENDĄ – IMS Bordeaux
- 03.** “Molecular engineering of hole transporting molecules for high efficient and enhanced thermal stability perovskite solar cell”
Thanh-Tuân BUI – LPPI
- 04.** “Structural and optoelectronics properties of gold based double perovskites semiconductors”
Géraud DELPORT – CNRS IPVF
- 05.** “Thermal and photo-degradation study of α -FAPbI₃-based perovskite using in situ characterization techniques”
Julie RUELLOU – LRCS
- 06.** “Colloidal Carbon Quantum Dots for More Stable Perovskite Solar Cells”
Dongjiu ZHANG – LPEM
- 07.** “Spectral fingerprint of quantum confinement in single CsPbBr₃ nanocrystals”
Mohamed-Raouf AMARA – LPENS
- 08.** “Electron's Spin Selectivity in Chiral Lead-Bromide Perovskites”
Alexandre ABHERVÉ – MOLTECH-Anjou
- 09.** “Excitons in highly anisotropic lead halide perovskite nanocrystals”
Maria CHAMARRO – INSP
- 010.** “Innovative approaches of film processing and interfacial structuration of CH₃NH₃PbI₃ and Cs₂AgBiBr₆ perovskite solar cells towards enhanced light absorption”
Anthony MAHO – ICMCB
- 011.** “Photo-physical Properties of Graphene Quantum Dots on Perovskite Substrates”
Hugo LEVY-FALK – ENS Paris-Saclay



- O12.** “Shedding light on the birth of hybrid perovskites: a correlative study by In-Situ TEM and synchrotron-based X-Ray scattering studies”
Charles SIDHOUM – IPCMS
- O13.** “Fabrication of green light-emitting diodes using CsPbBr₃ perovskite nanocrystals embedded in polymer matrices”
Quang-Huy DO – XLIM
- O14.** “ground-breaking PEROvskite technologies for advanced X-ray medical Imaging Systems”
Eric GROS-D’AILLON – CEA LETI
- O15.** “Influence of surface ligands on the electronic properties of AgBiI₄ rudorffites nanocrystals”
Ashanti BERGONZONI – INSA Rennes
- O16.** “Room temperature synthesis of green emitting lead-free perovskite inspired manganese halides”
Pierre MARTIN – Université Clermont Auvergne
- O17.** “Long-range and ballistic propagation at room temperature of 75% excitonic fraction polaritons in perovskite metasurface”
Hai Son NGUYEN – INSA Lyon & LuMIn
- O18.** “Deep-learning assisted identification of new hybrid perovskites from X-ray diffraction patterns”
Romain GAUTIER – IMN Jean Rouxel
- O19.** “Donor-Acceptor Pair Transitions in Halide Perovskite CH₃NH₃PbI₃ Single Crystals”
Thi Huyen Trang NGUYEN – UVSQ
- O20.** “Tight-binding modelling of layered halide perovskites”
Simon Thébaud – INSA Rennes
- O21.** “Detailed Analysis and Modelling of the Photocurrent Response of MAPb(Br_{1-x}Cl_x)₃ Single Crystals under X-rays”
Ferdinand Lédée – CEA LETI
- O22.** “Elaboration of new hybrid perovskite@graphite composites and mixed 2D/3D perovskites with enhanced stability for X-ray detection via a solvent-free mechanochemical approach”
Yihui CAI – ICPEES



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Perovskite-based NIR photodetectors

L. Paillardet^{1,2,3}, S. Charlot¹, K. Lambert¹, O. Gourhant³, B. Mortini³, D. Aldakov², J-M. Verilhac¹

¹ Grenoble Alpes University, CEA, LITEN, DTNM, F38000 Grenoble, France

² Grenoble Alpes University, CNRS, CEA, INP, IRIG/SYMMES, F38000 Grenoble, France

³ STMicroelectronics, Digital Front End Manufacturing & Technology, Crolles, France

Type of communication: Oral

Sensors in the near-infrared (NIR) range have attracted high attention due to the increasing need for 3D imaging and facial recognition technologies. The current near-infrared photodetectors are based on crystalline silicon photodiodes which suffers from low absorption coefficient in the near infrared. In this context, it has become necessary to investigate alternative photodetector materials. Among the candidates, the halogenated perovskites have high absorption coefficient as well as unique properties that could be tuned by their chemical composition. It has been demonstrated that partial replacement of lead with tin can lower the bandgap of halogenoplumbate perovskite through the so-called “bowing effect” [1]. An optimized molar ratio of lead to tin (1:1) lowers the bandgap down to ~1.16 eV. The latter paired with a high absorption coefficient at 940 nm would enable efficient photodetection in the NIR.[2]

Motivated by this approach, we developed a solution-processed mixed cation lead-tin perovskite ($\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$) thin film (~500 nm) integrated in a *p-i-n* photodetector device. The perovskite layer is fabricated in controlled atmosphere by spin coating and dried with anti-solvent treatment followed by a thermal annealing. To further enhance the stability of the binary lead-tin perovskite to oxidation, SnF_2 was used as an additive. We will discuss how the solvents engineering could affect the morphology and crystalline orientation of the thin perovskite layer. Optimized devices exhibit an external quantum efficiency of ~45% at 940 nm and a low dark current of ~20 nA/cm². Such performances were obtained on multiple devices, nevertheless, despite the precautions, some lack of reproducibility has been observed from batch to batch. Deeper investigation by XPS shows that the performances variability could be attributed to the high sensitivity of tin precursor towards oxidation. A solution is proposed to overcome this problem by using a pre-treatment of tin precursor with a metallic tin wire [3]. Such approach efficiently mitigates the detrimental Sn^{2+} to Sn^{4+} oxidation and leads to more robust process and photodiodes performances.

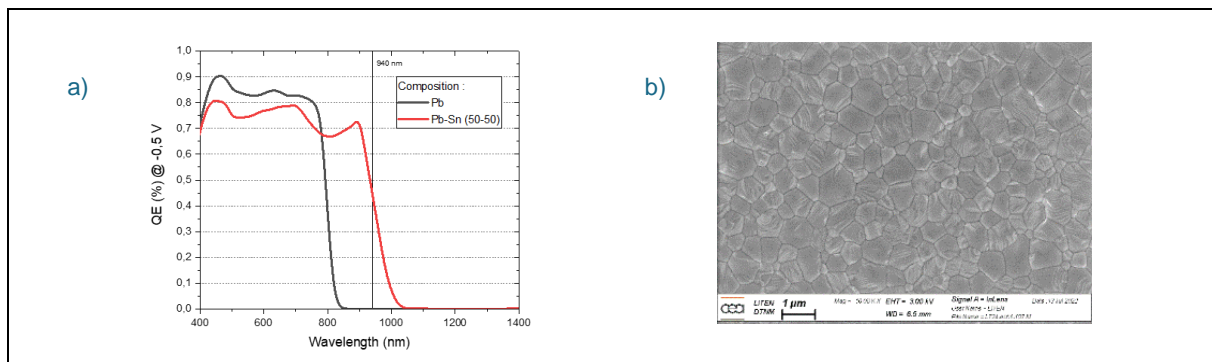


Figure 1: a) (left) External Quantum efficiency of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ and $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}_{0.5}\text{I}_3$ perovskite-based photodetector at -0.5 V bias b) (right) SEM image of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ perovskite film



JPH 2023

Journées Perovskites Halogénées

📅 31/05 – 02/06 📍 Biarritz, France

References

- [1] A. Goyal, S. McKechnie, D. Pashov, W. Tumas, M. Van Schilfgaarde, and V. Stevanović, “Origin of Pronounced Nonlinear Band Gap Behavior in Lead-Tin Hybrid Perovskite Alloys,” *Chem. Mater.*, vol. 30, no. 11, pp. 3920–3928, 2018, doi: 10.1021/acs.chemmater.8b01695.
- [2] L. Mei *et al.*, “Hybrid Halide Perovskite-Based Near-Infrared Photodetectors and Imaging Arrays,” *Adv. Opt. Mater.*, vol. 10, no. 9, 2022, doi: 10.1002/ADOM.202102656.
- [3] A. Morteza Najarian *et al.*, “Sub-millimetre light detection and ranging using perovskites,” *Nat. Electron.*, vol. 5, no. 8, pp. 511–518, 2022, doi: 10.1038/s41928-022-00799-7.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 — Biarritz, France

Redox-active substitutional doping of metal halide perovskites

Zuzanna Molenda^{a,b}, Sylvain Chambon^a, Dario Bassani^b, Lionel Hirsch^a

a) Univ. Bordeaux, CNRS, Bordeaux INP, IMS, UMR 5218, F-33400 Talence, France

b) Univ. Bordeaux, CNRS, Bordeaux INP, ISM UMR 5255, F-33400 Talence, France

Type of communication: Oral

Controlled doping of metal halide perovskites will increase their applicability in devices such as solar cells, LEDs, photodetectors or transistors. However, perovskite doping appears to be a challenge, due to ionic character of the perovskite crystal and its famous “defect tolerance”. We show that redox-active ions, such as Sm^{2+} , can substitute Pb^{2+} in MAPbI_3 (MA = methylammonium) and oxidize to Sm^{3+} , once incorporated into the crystal lattice. The electron released from each oxidizing ion becomes a free charge carrier in the conduction band. The oxidation of samarium ions is confirmed by the Sm 3d core level in the X-ray photoelectron spectrum (XPS) analysis. Residual content of the oxidized form of Sm^{3+} present in the doping solution, allows to observe a slight shift of the Sm 3d peak towards higher binding energy, suggesting the environment change of the Sm^{3+} ion, once it is introduced inside the perovskite film. This supports the hypothesis that the dopant ion is incorporated and stabilized in the crystal lattice. At the same time crystal structure of the doped perovskite layers is conserved and no phase separation is observed at the XRD patterns. The analysis of the ultraviolet photoelectron spectroscopy (UPS) shows the shift of the Fermi level (E_F) by around 0.5 eV towards the conduction band, proving the doping to be n-type. The increase of the free electron density in the conduction band is the direct reason for the conductivity increase for the doped films by 3 orders of magnitude. Using the Mott-Schottky method we estimated the ionized charge carrier density to be 10^{17} cm^{-3} for the sample showing the highest conductivity increase, which suggests the ionized dopant concentration in the doped perovskite film to be around 0.1% (Pb density in $\text{MAPbI}_3 \approx 20^{21} \text{ cm}^{-3}$). The discrepancy between this result and the doping concentration stemming from the XPS measurement, which is calculated to be around 20%, lead to investigate the dopant activation energy that can be calculated from the Arrhenius plot of the conductivity vs. temperature measurement. We found that the dopant activation energy is around 350 meV, which is in correspondence with the energy between the E_F and the conduction energy, i.e. this is the energy necessary to ionize all the dopants. This raises the possibility of the dopant freeze-out effect at room temperature, which could be responsible for only partial dopant activation in normal conditions.

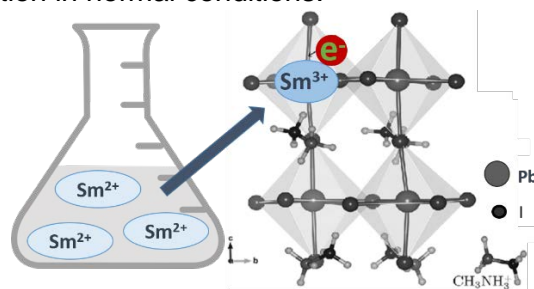


Figure 1. Scheme of the perovskite doping method using redox-active samarium ions.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Molecular engineering of hole transporting molecules for high efficient and enhanced thermal stability perovskite solar cell

Seul-Gi Kim^{a,b}, Thi Huong Le,^c Thybault de Monfreid^c, Jeong-Hyeon Kim^b, Fabrice Goubard^c, Joseph J. Berry,^{d,e,f} Kai Zhu^a, & Nam-Gyu Park^{b,g} Thanh-Tuân Bui^{c,*}

^aChemistry and Nanoscience Center, National Renewable Energy Laboratory, Golden, CO 80401, USA

^bSchool of Chemical Engineering and Center for Antibonding Regulated Crystals, Sungkyunkwan University, Suwon 16419, Republic of Korea

^cCY Cergy Paris Université, LPPI, F-95000 Cergy, France

^dMaterials Science Center, National Renewable Energy Laboratory, Golden, CO 80401, USA.

^eRenewable and Sustainable Energy Institute, University of Colorado Boulder, Boulder, CO 80309, USA

^fDepartment of Physics, University of Colorado Boulder, Boulder, CO 80309, USA

^gSKKU Institute of Energy Science and Technology (SIEST), Sungkyunkwan University, Suwon 16419, Republic of Korea

Corresponding author: T T Bui (tbui@cyu.fr)

Type of communication: Oral

We report here the design and synthesis of different series of conjugated molecules for use as charge transporting materials in halide perovskite solar cells. The thermal, morphological, optical and electrochemical properties of all prepared compounds have been investigated in detail and a comparative discussion has been presented. 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 %. Selected molecules have been subjected for further device optimization and in deep interface engineering (between the perovskite and hole transport layers) improving PCE to higher than 23 % and this champion PCE is even higher than that of the Spiro-OMeTAD-based device. Thermal stability test at 85 °C for over 1000 h showed that the PSC employed novel HTM retains 86% of initial PCE, while the Spiro-MeOTAD-based PSC degrades unrecoverably. 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. Under optimized condition, the perovskite solar cells employed additive-free HTM gave a PCE of ca. 16%. 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.

Reference:

1. 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, *Advanced Materials* **2021**, *33*, 2007431.
2. S.-G. Kim, T. de Monfreid, J.-H. Kim, F. Goubard, J. J. Berry, K. Zhu, **T.-T. Bui**, N.-G. Park, Manuscript Submitted



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Structural and optoelectronics properties of gold based double perovskites semiconductors

Géraud Delport¹, Alexandre Py¹, Philip Schulz¹, Jean-François Guillemoles¹

1: CNRS, Institut Photovoltaïque d'Île de France (IPVF), UMR 9006, 18, Boulevard Thomas Gobert, 91120 Palaiseau, France

Type of communication: Oral

Over the past years the family of halide perovskites crystals have been vastly investigated to design thin film based optoelectronics devices for applications such as solar cells, lights emitting diodes... One major advantage of halide perovskite with respect to conventional semiconductors is their chemical versatility that allows us to finely tune many of their optoelectronic properties. However conventional lead based perovskites suffer from many drawbacks, including toxicity and poor stability.

In this context, double perovskite and in particular gold based double perovskite $\text{Cs}_2\text{Au}_2\text{X}_6$ stand out as promising alternatives. In this presentation, I will detail our recent advances on the preparation in terms of powders and thin films. I will also detail the characterization of the structural and optical properties of such materials.

References

- [1] S.S. Hafner, N. Kojima, J. Stanek, Li Zhang, Divalent gold in perovskite type CsAuI_3 , Physics Letters A, Volume 192, Issues 5–6, 1994, Pages 385-388 [2] xxx
[2] Ghosh, B., Febriansyah, B., Harikesh, P. C., Koh, T. M., Hadke, S., Wong, L. H., ... & Mathews, N. (2020). Direct Band Gap Mixed-Valence Organic–inorganic Gold Perovskite as Visible Light Absorbers. Chemistry of Materials, 32(15), 6318-6325



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Thermal and photo-degradation study of α -FAPbI₃-based perovskite using *in situ* characterization techniques

[Julie RUELLOU](#)¹, Matthieu COURTY¹, Hervé VEZIN², Hania AHOURI², Frédéric SAUVAGE^{1*}

¹Laboratoire de Réactivité et Chimie des Solides, CNRS UMR7314, Université de Picardie Jules Verne, Hub de l'énergie, 15 Rue Baudelocque, 80039 Amiens Cedex, France

²Laboratoire de Spectroscopie pour les Interactions, la Réactivité et l'Environnement, CNRS UMR8516, Université de Lille, Campus de la cité scientifique de Villeneuve d'Ascq (bâtiment C4), 59655, Villeneuve-d'Ascq, France

Type of communication: Oral

Hybrid halide perovskite has established its credibility as high performance thin film photovoltaic technology. In only one-decade, the hybrid organic-inorganic halide perovskite solar cell achieved to compete with all mature crystalline technologies, by reaching a certified 25.7 % power conversion efficiency (PCE) on cells and 17.9 % PCE on small modules.¹ Perovskite's strength stem from their remarkable opto-electronic properties. However, the technology still requires significant considerations regarding stability issues which may engender rapid degradation under various external stressors (temperature^{2,3}, humidity⁴⁻⁶, light^{7,8}, electrical bias⁹).

To cope with the stability issue, it is mandatory to precisely understand the multiple degradation pathways of the perovskite. *In situ* or operando characterization techniques are key tools to probe the pathways of degradation. In this communication, we will be discussing the degradation of α -FAPbI₃ on the basis of temperature-controlled *in situ* x-ray diffraction (figure 1) and corroborated with *in situ* electron spin resonance spectroscopy. In particular, the first key finding which we will discuss is that α -FAPbI₃ degradation is substantially accelerated when temperature is combined to illumination and when it is interfaced with the extraction layers, and, second the existence of a temperature gap region which takes place only under illumination involving an intermediate stage between the thermal-induced perovskite degradation and the formation of PbI₂ by-product.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

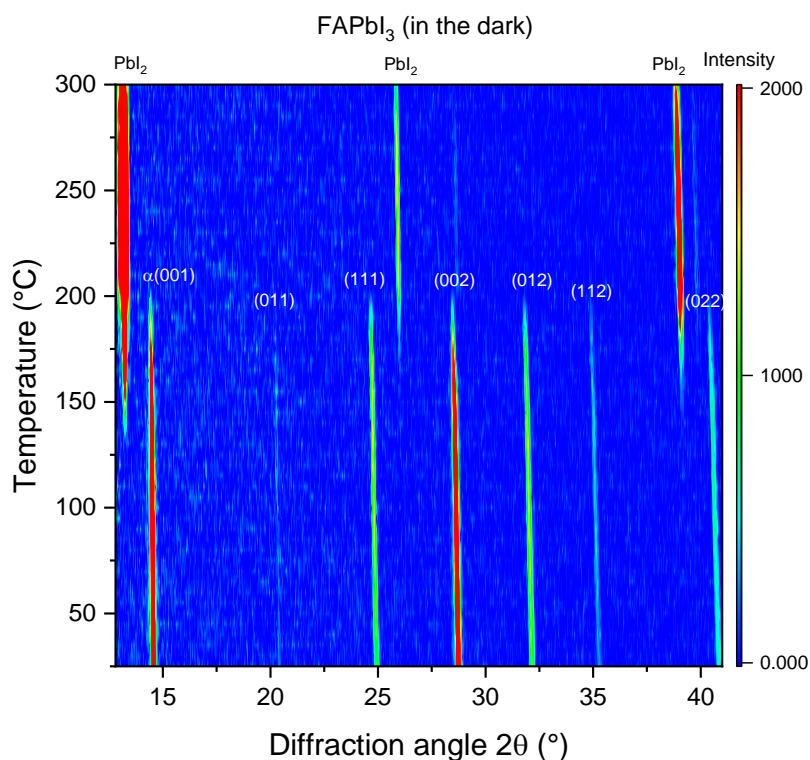


Figure 1.

References

- [1] NREL, P. research. *Best Research Cell Efficiency Chart*. <https://www.nrel.gov/pv/cell-efficiency.html> (accessed 2022-03-01).
- [2] Ava, T. T.; Al Mamun, A.; Marsillac, S.; Namkoong, G. A Review: Thermal Stability of Methylammonium Lead Halide Based Perovskite Solar Cells. *Applied Sciences* **2019**, *9* (1), 188. <https://doi.org/10.3390/app9010188>.
- [3] Ma, L.; Guo, D.; Li, M.; Wang, C.; Zhou, Z.; Zhao, X.; Zhang, F.; Ao, Z.; Nie, Z. Temperature-Dependent Thermal Decomposition Pathway of Organic–Inorganic Halide Perovskite Materials. *Chem. Mater.* **2019**, *31* (20), 8515–8522. <https://doi.org/10.1021/acs.chemmater.9b03190>.
- [4] Lin, Z.; Zhang, Y.; Gao, M.; Steele, J. A.; Louisia, S.; Yu, S.; Quan, L. N.; Lin, C.-K.; Limmer, D. T.; Yang, P. Kinetics of Moisture-Induced Phase Transformation in Inorganic Halide Perovskite. *Matter* **2021**, *4* (7), 2392–2402. <https://doi.org/10.1016/j.matt.2021.04.023>.
- [5] Akman, E.; Shalan, A. E.; Sadegh, F.; Akin, S. Moisture-Resistant FAPbI₃ Perovskite Solar Cell with 22.25 % Power Conversion Efficiency through Pentafluorobenzyl Phosphonic Acid Passivation. *ChemSusChem* **2021**, *14* (4), 1176–1183. <https://doi.org/10.1002/cssc.202002707>.
- [6] Akhavan Kazemi, M. A.; Raval, P.; Cherednichekno, K.; Chotard, J.-N.; Krishna, A.; Demortiere, A.; Reddy, G. N. M.; Sauvage, F. Molecular-Level Insight into Correlation between Surface Defects and Stability of Methylammonium Lead Halide Perovskite Under Controlled Humidity. *Small Methods* **2021**, *5* (2), 2000834. <https://doi.org/10.1002/smt.202000834>.
- [7] Emelianov, N. A.; Ozerova, V. V.; Zhidkov, I. S.; Korchagin, D. V.; Shilov, G. V.; Litvinov, A. L.; Kurmaev, E. Z.; Frolova, L. A.; Aldoshin, S. M.; Troshin, P. A. Nanoscale



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Visualization of Photodegradation Dynamics of MAPbI₃ Perovskite Films. *J. Phys. Chem. Lett.* **2022**, *13* (12), 2744–2749. <https://doi.org/10.1021/acs.jpcllett.2c00497>.

[8] Akbulatov, A. F.; Luchkin, S. Yu.; Frolova, L. A.; Dremova, N. N.; Gerasimov, K. L.; Zhidkov, I. S.; Anokhin, D. V.; Kurmaev, E. Z.; Stevenson, K. J.; Troshin, P. A. Probing the Intrinsic Thermal and Photochemical Stability of Hybrid and Inorganic Lead Halide Perovskites. *J. Phys. Chem. Lett.* **2017**, *8* (6), 1211–1218. <https://doi.org/10.1021/acs.jpcllett.6b03026>.

[9] Anoop, K. M.; Khenkin, M.; Di Giacomo, F.; Galagan, Y.; Rahmany, S.; Etgar, L.; Katz, E.; Visoly-Fisher, I. Bias-Dependent Stability of Perovskite Solar Cells Studied Using Natural and Concentrated Sunlight. *Solar RRL* **4** (1900335).



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Colloidal Carbon Quantum Dots for More Stable Perovskite Solar Cells

Dongjiu Zhang, Zhelu Hu, Chenghao Xin, Jiazhuo Nie, Lionel Aigouy, and Zhuoying Chen

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

Corresponding author: zhuoying.chen@espci.fr

Abstract: Organic-inorganic hybrid perovskite solar cells (PSCs) have exhibited excellent photovoltaic performance comparable to conventional silicon solar cells, except for their non-negligible poor long-term stability induced by various environmental factors (e.g., moisture, oxygen, and ultraviolet (UV) light). In particular, the perovskite absorber layer has been found to undergo various degrees of degradation due to UV radiation. To address this issue, in this work, we investigate the possibility to harvest the unique optical property of colloidal carbon quantum dots (CQDs) on perovskite solar cells. To this aim, uniform UV absorbing and visible emitting CQDs were synthesized. Thorough structural and optical characterizations were performed on them. Finally, they were applied onto functional perovskite solar cells as a UV protection and down-shifting layer and we studied the effect of CQDs on the degradation behavior of the solar cells under UV illumination. Under an identical UV degradation condition, optimized CQD-protected perovskite solar cells exhibited only 5% of PCE drop after 100 hours of UV exposure (in air) in comparison to control devices (without CQDs) which exhibited > 50% of PCE drop after 40 hours.

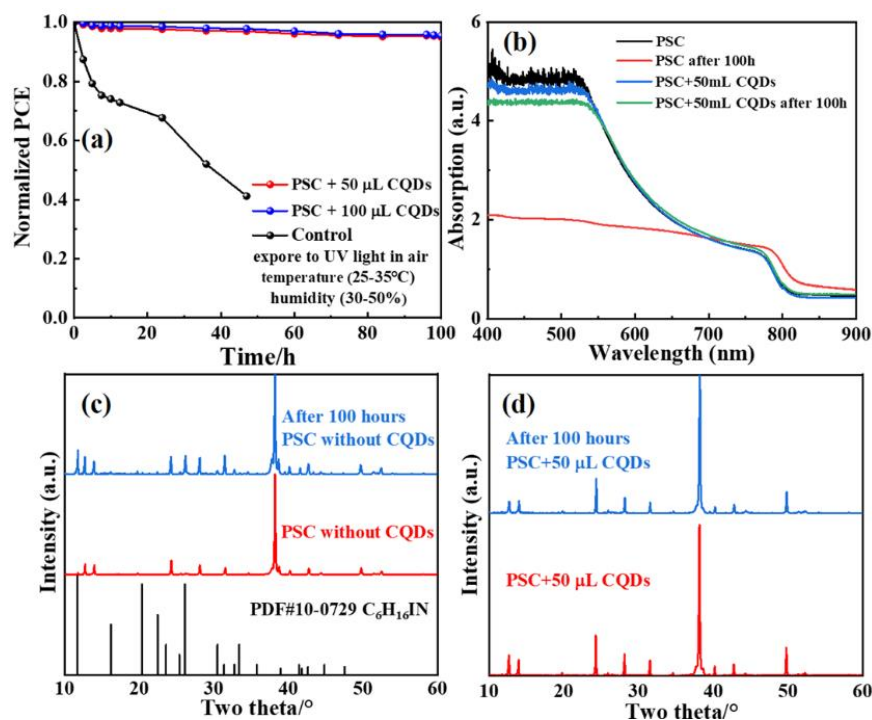


Figure 1. a) Normalized stability of the PSCs without CQDs and with 50 μ L and 100 μ L CQDs layer after 100 hours of continuous exposure to UV light ($\lambda = 365$ nm, 5 mW cm^{-2}) in air. b) Absorption spectrum of PSC without CQDs, with 50 μ L CQDs and the other two after 100 hours of continuous exposure to UV light in air. c) XRD patterns of PSC without CQDs before and after 100 hours of continuous exposure to UV light in air. d) XRD patterns of PSC with 50 μ L CQDs before and after 100 hours of continuous exposure to UV light in air.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Spectral fingerprint of quantum confinement in single CsPbBr₃ nanocrystals

M.-R. Amara^{1,2,*}, Z. Said¹, C. Huo², A. Pierret¹, C. Voisin¹, W. Gao², Q. Xiong^{2,3} and C. Diederichs^{1,4}

¹ *Laboratoire de Physique de l'École Normale Supérieure, ENS, PSL, CNRS, Sorbonne Université, Université de Paris, 75005 Paris, France*

² *Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore*

³ *State Key Laboratory of Low-Dimensional Quantum Physics and Department of Physics, Tsinghua University, Beijing 100084, China*

⁴ *Institut Universitaire de France (IUF)*

Type of communication: Oral

Lead halide perovskite NCs (LHP NCs) are a promising class of materials for various optoelectronic applications related to light absorption and emission. Because of their defect-tolerant nature, LHP NCs remain bright without the need of core-shell structures and the emission can be tuned over the entire visible range by a combination of size-engineering, i.e. quantum confinement and composition-engineering.

Critical information on these materials can be sought from the band-edge exciton fine structure (EFS) which can be revealed in low-temperature single NC experiments. Early studies of individual LHP NCs have reported narrow lines grouped in doublets or triplets attributed to a bright triplet exciton together with several additional peaks attributed to the charged exciton, biexciton and phonon replicas [1]. Theoretically, the EFS of these materials has been the subject of an intense debate in the community since the prediction that the Rashba effect should place the bright triplet exciton as the ground exciton state [2]. While this prediction was since contradicted [3], the discussion has now shifted towards quantifying the influences of the exchange interaction and this potential Rashba effect [4].

Here, we report on a comprehensive study of the spectral properties of more than 200 individual CsPbBr₃ nanocrystals at cryogenic temperature with edge lengths from 5 to ~25 nm. The spectral fingerprint of quantum confinement in the band-edge EFS emission is revealed via the features of the triplet exciton, charged exciton, biexciton, and their phonon replicas.

The diversity of bright triplet exciton spectra is rationalized and bright-bright energy splittings reveal a general increase with confinement, consistent with a pure exchange model (i.e. no signature of the Rashba effect). Similarly, the charged exciton and biexciton binding energies are consistent with a simple quantum confinement model. For each exciton complex, we also evidence the emission of up to four phonon replicas whose energies do not depend on the NC size, while the exciton-phonon coupling strength increases with confinement.

This work provides a detailed study of quantum confinement in individual CsPbBr₃ NCs which will feed the scientific debate and help refine models to converge towards a realistic description of the EFS of these promising materials.

References

- [1] Fu et al., *Nano Letters* **5**, 2895 (2017) ; Ramade et al., *Nanoscale* **14**, 6393 (2018)
- [2] M. Becker et al., *Nature* **553**, 189 (2018)
- [3] Tamarat et al., *Nat Mat* **7**, 717 (2019) ; *Nat. Comm.* **1**, 6001 (2020)
- [4] Ben Aich et al., *PRA* **3**, 034042 (2019); *JPC* **11**, 808 (2020); Sercel et al., *Nano Letters* **6**, 4068 (2019); *JCP* **23**, 234106 (2019)



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Electron's Spin Selectivity in Chiral Lead-Bromide Perovskites

Alexandre Abhervé,¹ Mikaël Kepenekian,² Claudine Katan,² Jacky Even,³ Anil Kumar,⁴ Tapan Kumar Das,⁴ Nicolas Mercier,¹ Ron Naaman⁴

¹Laboratoire MOLTECH-Anjou, Université d'Angers, France

²Institut des Sciences Chimiques de Rennes, Université de Rennes, France

³Institut National des Sciences Appliquées de Rennes, France

⁴Department of Chemical and Biological Physics, Weizmann Institute of Science, Israel

Type of communication: Oral

By combining the optoelectronic properties of halide perovskites (HPs) with chirality transfer from inserted organic cations, chiral HPs brought new perspectives for chiroptical and spintronic applications.^[1] For example, the emergent field of chiro-spintronics proposes to use chiral molecules as a substitute for ferromagnetic materials thanks to the spin-specific interaction between electrons and chiral molecules, a phenomenon called CISS, “chirality-induced spin selectivity”. Following this strategy, we prepared a series of chiral lead-bromide networks which crystallize in enantiomorphic polar space groups $P4_12_12$ and $P4_32_12$ for the R and S enantiomers respectively. An in-depth theoretical study on their band structure and spin texture revealed the impact of such symmetry elements on the spin selectivity of this family of molecular materials. Furthermore, CISS effect measurements have been performed by magnetic conducting-probe atomic force microscopy (mc-AFM) and revealed a spin polarization of about 40% in our materials. Therefore, we fabricated a chiro-spintronic device with each enantiomer. Inversion of the sign of the magnetoresistance can be observed depending on the direction of the applied magnetic field and the nature of the enantiomer. Such spin valve devices show a signal independent to the external temperature from 5 K to 250 K, showing the possibility of using iodide-free HP materials for spintronic devices.

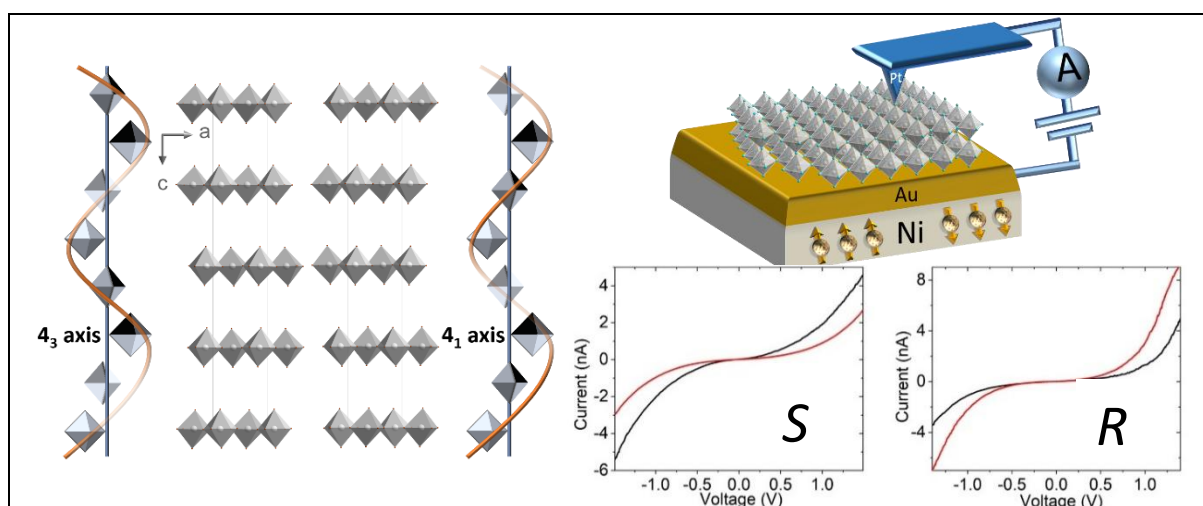


Figure 1. Left: Partial view of the crystal structures with illustration of the 4_3 and 4_1 symmetry elements. Right: Schematic representation and results of mc-AFM measurements for S and R enantiomers.

References

[1] Lu, H.; Vally Vardeny, Z.; Beard, M. C., *Nat. Rev. Mater.* **2022**, 6, 470-485.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Excitons in highly anisotropic lead halide perovskite nanocrystals

Victor Guilloux¹, Amal Ghribi², Rim Ben Aich², Kaïs Boujdaria², Thierry Barisien¹, Laurent Legrand¹, Emmanuel Lhuillier¹, Christophe Testelin¹ and Maria Chamorro¹

1-Institut des NanoSciences de Paris, CNRS UMR 7588, Sorbonne Université, F-75005 Paris, France;

2-LR01ES15 Laboratoire de Physique des Matériaux: Structure et Propriétés, Faculté des Sciences de Bizerte, Université de Carthage, Bizerte 7021, Tunisia;

Type of communication: Oral

Lead halide perovskites have attracted the attention of the research community due to their outstanding opto-electronic properties. Moreover, chemical synthesis of colloidal materials has opened the path to a large panel of nanostructures with various shapes and confinement geometries.

In this work, we study the excitonic band edge states of the inorganic perovskite with highly anisotropic shape: the analogous to the quantum wells fabricated by MBE techniques and called nanoplatelets (NPLs)[1]. We address, particularly, the importance of dielectric mismatch effects in exciton main properties, i.e. binding energy and fine structure [2].

The dielectric effects are outstandingly strong in NPLs. As in other thin 2D systems, the exciton binding energy increases dramatically as thickness of NPLs are reduced: from 36 meV in bulk CsPbBr₃, to about 200 meV for NPLs with a monolayer thickness. That is the result of the combined effect of a strong 2D confinement and a reduced dielectric screening.

The fine structure consists on four excitonic states with one dark state (D) at lower energy and three bright excitonic states (B), fully degenerated in nanocrystals with cubic-shape and cubic crystal phase [3]. However in NPLs, two groups of B-excitons are distinguished due to the electronic confinement: those with dipole in the plane of the NPL and those with dipole perpendicular to the plane. The latter ones are less coupled with the light due to dielectric screening.

We discuss and compare our theoretical results with the experimental data for CsPbBr₃ NPLs. A good agreement is found.

References

- [1] S. T. Ha, et al, Adv. Optical Mater., 2014, **2**, 838-844.
- [2] Ghribi A. et al, Nanomaterials, 2021, **11**, 3054
- [3] Ben Aich R., et al, J. of Phys. Chem. Lett. 2020, **11**,808.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Innovative approaches of film processing and interfacial structuration of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{Cs}_2\text{AgBiBr}_6$ perovskite solar cells towards enhanced light absorption

Anthony Maho*, Nathan Daem, Gilles Spronck, Pierre Colson,
Rudi Cloots and Jennifer Dewalque

GREENMat (UR CESAM), Université de Liège, 13 Allée du Six-Août, 4000 Liège, Belgium

**Now at Univ. Bordeaux, CNRS, Bx INP, ICMCB (UMR 5026), 87 Avenue du Dr Schweitzer, 33600 Pessac, France*

Type of communication: Oral

This contribution first covers the use of polystyrene beads as hard templating sacrificial agents for the design of inverse-opal electron-conducting TiO_2 [1] and of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite porous layers [2] through spin coating protocols, from which full solid-state architectures of perovskite solar cells are consecutively assembled. The positive effect of the porous structuration of the photoactive layers in comparison with dense, unstructured counterparts is demonstrated. Moreover, the specific impact of the pore dimensions on the morphological and optoelectronic properties of the structured layers is studied through structural (SEM, XRD), optical (UV-VIS-NIR, ellipsometry) and electronic/electrochemical analyses (I-V curves, EIS). The influence of the photon absorption intensity and lifetime on the charge recombination mechanisms within structured and unstructured active layers is further discussed. Ultimately, optimums of structural configurations are experimentally established in terms of light harvesting and of power conversion efficiency, in good correspondence with numerical studies [3,4]. Maximized light absorption is reached for 500 nm diameter pores structure, with photonic enhancement factors as high as 9% with inverse opal TiO_2 photoanodes and 16% with inverse opal perovskite layers, compared to unstructured compact benchmarks.

As other formulation of interest for solar cells, $\text{Cs}_2\text{AgBiBr}_6$ double perovskite is considered as a promising alternative, lead-free photovoltaic absorber due to its easy processability, high stability, and reduced toxicity. In this context, our recent works have shown that spray-coating could be used advantageously for depositing high quality $\text{Cs}_2\text{AgBiBr}_6$ double perovskite thin films [5]. Microstructural and optoelectronic properties of spray-coated layers are compared with spin-coated benchmarks, and consecutively assembled devices lead to 2.3% photoconversion efficiency with high open-circuit voltage of 1.09 V. Further optimization is considered through the design of combined layers of tetracene and Spiro-OMeTAD so to strengthen the perovskite - hole transport material interface [6].

References

- [1] A. Maho *et al.*, ACS Applied Energy Materials 2021 4 1108, DOI: 10.1021/acsaem.0c02124
- [2] N. Daem *et al.*, ACS Applied Nano Materials 2022 5 13583, DOI: 10.1021/acsanm.2c03274
- [3] M. Lobet *et al.*, Optics Express 2019 27 32308, DOI: 10.1364/OE.27.032308
- [4] M. Lobet *et al.*, Applied Sciences 2020 10 1783, DOI: 10.3390/app10051783
- [5] N. Daem *et al.*, Solar RRL 2021 5 2100422, DOI: 10.1002/solr.202100422
- [6] N. Daem, J. Dewalque, D. K. Kim, G. Spronck, C. Henrist, P. Colson, S. Heutz, R. Cloots, and A. Maho. Improved photovoltaic performance of lead-free $\text{Cs}_2\text{AgBiBr}_6$ double perovskite solar cells incorporating tetracene as co-hole transport layer. In preparation 2023.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Photo-physical Properties of Graphene Quantum Dots on Perovskite Substrates.

[Hugo Levy-Falk](#)¹, Thanh Trung Huynh¹, Thomas Liu¹, Daniel Medina-Lopez², Silvio Osella³, David Beljonne⁴, Stéphane Campidelli², Loïc Rondin¹, Jean-Sébastien Lauret¹, and Emmanuelle Deleporte¹

¹ *Université Paris-Saclay, ENS Paris-Saclay, CentraleSupélec, CNRS, LuMIn, Orsay, France*

² *Université Paris-Saclay, CEA, CNRS, NIMBE, LICSEN, 91191 Gif-sur-Yvette, France*

³ *Chemical and Biological Systems Simulation Lab, Centre of New Technologies, University of Warsaw, Banacha 2C, 02-097 Warsaw, Poland*

⁴ *CMN, Université MONS, Belgium*

Type of communication: Oral

Graphene quantum dots (GQDs) are a promising platform for building quantum light emitters. We have, for instance, shown that single GQDs are stable and bright single photon emitters[1]. Recently, the importance of vibration in their light emission process has been shown[2, 3]. In the perspective of exploiting the outstanding properties of GQDs, a path to be explored is to couple them with other active materials.

In this context, lead-halide hybrid perovskites are a family of semiconductors holding great promise for photovoltaic, light-emitting devices, and laser applications. High-quality crystals can be synthesized at room temperature by soft chemistry[4], providing a desirable and easy-to-use semiconductor substrate candidate.

In the present work, we will first present the photo-physical properties of new GQDs structures showing a high solubility and fluorescence quantum yield up to 94%[5]. Then we will report on a study of the coupling of these GQDs to micrometer-thick methylammonium lead bromide perovskite single crystals down to a single molecule. In particular, we will compare the stability of the GQDs photoluminescence on those substrates against their stability when embedded in a polymer matrix.

References

- [1] S. Zhao et. al., Nature Communications, 9, 3470 (2018)
- [2] T. Liu et. al., Nanoscale, 14, 3826 – 3833 (2022)
- [3] T. Liu et. al., Journal of Chemical Physics 156, 104302 (2022)
- [4] F. Lédée et. al., CrystEngComm, 2017, 19, 2598-2602
- [5] D. Medina Lopez et. al. Under Review



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Shedding light on the birth of hybrid perovskites: a correlative study by *In-Situ* TEM and synchrotron-based X-Ray scattering studies

Charles Sidhoum¹, Dris Ihiawakrim¹, Clément Sanchez², Doru Constantin³, Thomas Bizien⁴, Ovidiu Ersen¹

¹Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue Loëss, Strasbourg, France ; ²USIAS, University of Strasbourg Institut of Advanced Study, France ; ³Institut Charles Sadron, UPR22, 6 rue Boussingault, 67083 Strasbourg cedex, France ; ⁴Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin BP 48, Gif-sur-Yvette 911190, France

Type of communication: Oral

Ligand-assisted reprecipitation (LARP) approach is an easy pathway of synthesis to obtain lead halide perovskite¹. It presents the advantage of being done at room temperature by mixing two solvents with different polarities. DMF and DMSO are the two commonly used polar solvents for the preparation of the precursor mixture but lead to the obtention of an intermediate phase [2] before obtention, by annealing, of the final 3D perovskite phase. The accurate knowledge of the formation process by LARP, from the molecular precursors to the intermediate and final 3D phases, is paramount to be able to optimize the performances of these very promising hybrid materials. In this framework, we correlate synchrotron-based X-ray scattering experiments with liquid phase TEM (LP-TEM) to shed new lights on the nucleation and growth of these intermediate phases.

Using the LARP approach with DMF as polar solvent, we report the obtention of an intermediate (2MAI-3PbI₂-2DMF) phase, identified by XRD, with a needle-like morphology observed by TEM. Thanks to the recent development of LP-TEM, it is also possible to obtain a real time insight into the evolution of the reaction mixture and to observe what mechanisms occur during the formation. We observed the crystallization of the intermediate phase in solution under electron beam (Movie S1), showing the growth from an ellipsoidal shape (Figure 2. A-insert) to the needle-like final morphology (Figure 2. B-insert). This information is confirmed by reproducing the process during synchrotron-based SAXS experiments showing evolution of the reaction mixture from isotropic objects (Figure 2. A) to anisotropic shape (Figure 2. B) with similar time scale compared to LP-TEM experiments (insert in Figure 2). The formation of the intermediate phase by LARP was thus monitored which is, to our best knowledge, the first direct visualization at the nanoscale of such a metastable phase by TEM.

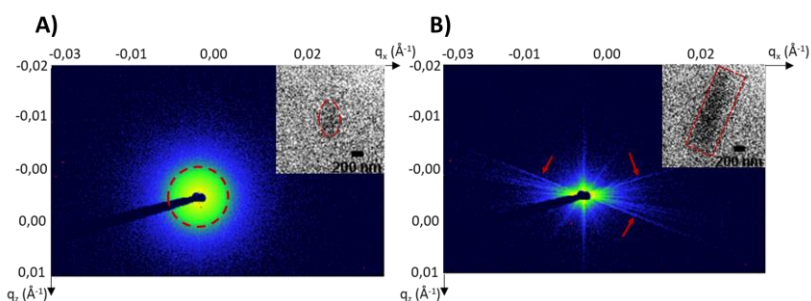


Figure 1. SAXS detector images acquired at: A) t+150ms; B) t+5000ms. The dotted red circles indicate the isotropic scattering signal; the red arrows indicate the anisotropic scattering signal. TEM images extract at t+150ms and t+5000ms from LP-TEM experiments are insert to show the morphology adopted by the system at these specific times in solution at the nanoscale. These both advanced *in-situ* techniques are in good agreement.

References

- [1] Shamsi, J. et al. Chem. Rev. 2019, 119 (5), 3296–3348
- [2] Petrov, A. et al. Journal of Physical Chemistry C 2017 121 (38), 20739-20743



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Fabrication of green light-emitting diodes using CsPbBr₃ perovskite nanocrystals embedded in polymer matrices

Quang-Huy Do¹, Cédric Mayer², Hugo Levy-Falk², Gaëlle Allard-Trippé², Bernard Ratier¹, Rémi Antony¹, Emmanuelle Deleporte², Johann Bouclé¹

¹ XLIM UMR CNRS 7252, Université de Limoges, Limoges, France

² LuMIn UMR CNRS 9024, Université Paris-Saclay, ENS Paris-Saclay, Centrale Supélec, Gif-sur-Yvette, France

Type of communication: Oral

Perovskite nanocrystals have gained attention for their potential use in optoelectronic applications due to their high luminance efficiency, color purity, and adjustable bandgap. A recent study by Cédric Mayer and colleagues in 2022 introduced a novel method for synthesizing large quantities of perovskite nanocrystals under ambient conditions without compromising their optical properties [1]. Here, we present a prototype of green light-emitting diodes fabricated using monodisperse CsPbBr₃ perovskite nanocrystals synthesized via this room-temperature soft-chemical process. Our focus was to integrate the perovskite nanocrystals into a poly(methyl methacrylate) (PMMA) polymer matrix to form the emissive layer of the device. The results showed that optimal performance was achieved when the mass ratio of perovskite nanocrystals to polymer was 10:1, resulting in a maximum brightness of 800 Cd/m² at the emission wavelength of 520 nm. Our work highlights the potential of using ambient-temperature-prepared perovskite nanocrystals in polymer matrices for sustainable and high-performance light-emitting devices.

References

[1] Cédric R. Mayer, Hugo Levy-Falk, Maxime Rémond, Gaëlle Trippé-Allard, Frédéric Fossard, Maxime Vallet, Marc Lepeltier, Nicolas Guiblin, Jean-Sébastien Lauret, Damien Garrot, Emmanuelle Deleporte. *Synthesis method of highly calibrated CsPbBr₃ nanocrystals perovskites by soft chemistry*. Chem. Commun., 2022,58, 5960-5963, <https://doi.org/10.1039/D2CC01028C>



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

ground-breaking PEROvskite technologies for advanced X-ray medical Imaging Systems

Eric Gros-Daillon, in behalf of the Peroxis consortium

Grenoble Alpes University, CEA, LETI, DOPT, F38000 Grenoble, France

X-ray flat panel detectors (FPD) are widely used for diagnostic of diseases but suffers from a lack of signal to noise ratio at low dose for cardiovascular imaging, such as visualization of moving stents, and temporal artefacts for 3D imaging and stroke detection. Direct detection should combine a high sensitivity and a high spatial resolution but has not been yet implemented in general radiography due to lack of satisfactory semi-conducting material. The sharp specifications required a combination of high-level optoelectronic properties, low temperature processing of thick (sub-100 μm) layer on large area, and cost-effective materials and processes. Developments in perovskite metal halide semiconductors over the last ten years have raised the prospect of achieving all these characteristics.

The H2020 PEROXIS project [1] aimed to develop a new generation of FPD based on direct X-ray to electron conversion thanks to perovskite semiconductor. A dedicated backplane (240 \times 240 pixel array) based on amorphous silicon technology has been designed. Two routes are followed to produce thick perovskite layers. The soft sintering of MAPI powder enabled to produce large area pellets, until 10 \times 10 cm². Several pellets were bonded to the backplanes thanks to a liquefied MAPI layer. Pixelated X-ray detector show high spatial resolution and good sensitivity (figure 1), despite the high level of the dark current and its instability. An alternative route is the growth of MAPbBr₃ polycrystalline grains by a process in solution. First images have been made from this technology but lack of spatial resolution, because of the grain size or because of the coupling layer between the perovskite film and the backplane. They also suffered from high dark current. Dark current in the MAPI pellet and MAPbBr₃ layers are intensively studied by impedance spectrometry and chronoamperometry. Moving ions or vacancies can naturally accumulate at the electrode upon biasing. Ionic currents are negligible in comparison to the electronic currents; however, they influence them via changes in the charge density profile, for both MAPI [2] and MAPbBr₃ [3] devices (figure 2).

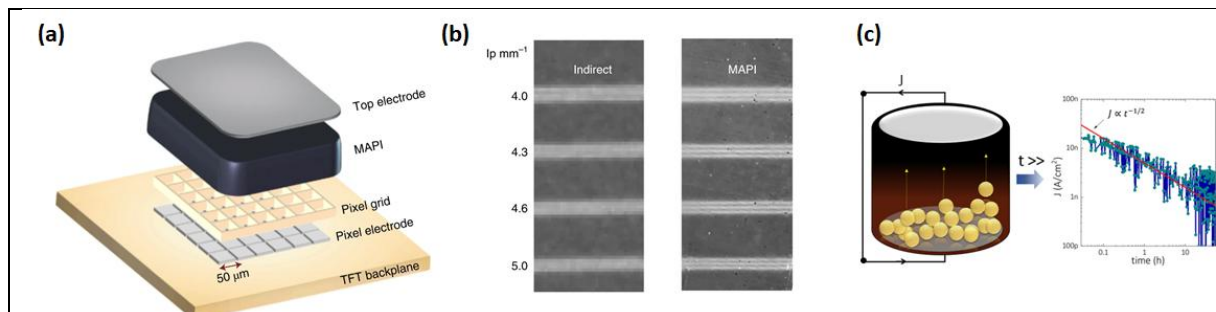


Figure 1. **a.** Exploded view of the different elements of the X-ray imager. **b.** X-ray image of a resolution pattern s taken by the indirect-conversion (left) and MAPbI₃ detector (MAPI; right). Figure taken from [1] Dark current versus time evolution is presumed to be caused by ion motion in MAPI (devices. Figures taken from [3].

References

[1] <https://peroxis-project.eu/>



JPH 2023

Journées Perovskites Halogénées

📅 31/05 – 02/06 📍 Biarritz, France

[2] Deumel, S. et al. Nat Electron 4, 681–688 (2021).

[3] Marisé García-Batlle et al., ACS Applied Materials & Interfaces 2021,



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Influence of surface ligands on the electronic properties of AgBiI₄ rudorffites nanocrystals

Ashanti Bergozoni^a, Anastasia Matuhina^b, G. Krishnamurthy Grandhi^b, Laurent Pedesseau^a, Jacky Even^a, Paola Vivo^b

a. Univ Rennes, INSA Rennes, CNRS, Institut FOTON – UMR 6082, F-35000 Rennes, France

b. Hybrid Solar Cells, Faculty of Engineering and Natural Sciences, Tampere University, P.O. Box 541, FI-33014 Tampere University, Finland

Type of communication: Oral

In the last decade, owing to a combination of outstanding optical and electronic properties, lead halide perovskite (LHP) have prevailed as promising low-cost materials for optoelectronic applications going from photovoltaics¹ to photocatalysis². However, within a time when ecology is the keystone of concerns, the presence of lead at the forefront of their structures and properties, as well as their operational instability, hindered their commercial applications^{3,4}.

In the sake of non-toxic alternatives, Ag-Bi-I Rudorffites have recently emerged as potential candidates. Indeed, in 2016, solar cells made from these materials showed a power conversion efficiency of 1.2%⁵, which has now increased to 5.4%⁶. With edges-shared AgI₆ and BiI₆ octahedra, Rudorffites have well-positioned band gap and high absorbance in the entire visible range, along with greater stability in ambient conditions than LHP⁶.

In this study, AgBiI₄ nanocrystals (NCs) have been synthesized via the hot-injection route. Interestingly, they show a quasi-direct band gap value closely matching the bulk material one. Alongside, surface characterization has shown the presence of ligands passivating the NCs' surface, suggesting an effect of the surface coverage on the electronic properties. Recent theoretical developments based on density functional theory (DFT), have uncovered the influence of surface dipoles on work functions in LHP⁷ and similar mechanisms might occur here. Up to date, this has not been demonstrated yet for Ag-Bi-I Rudorffites NCs. Therefore, expanding recent theoretical descriptions of Ag-Bi-I Rudorffite bulk properties⁸, we propose to combine DFT surface calculations with experimental results, to clarify the fundamental mechanisms behind the bandgap closing observed in these nanocrystals.

References

- (1) *Best Research-Cell Efficiency Chart*. <https://www.nrel.gov/pv/cell-efficiency.html> (accessed 2023-03-02).
- (2) Zhu, X.; Lin, Y.; San Martin, J.; Sun, Y.; Zhu, D.; Yan, Y. Lead Halide Perovskites for Photocatalytic Organic Synthesis. *Nat. Commun.* **2019**, *10* (1), 2843. <https://doi.org/10.1038/s41467-019-10634-x>.
- (3) Siegler, T. D.; Dawson, A.; Lobaccaro, P.; Ung, D.; Beck, M. E.; Nilsen, G.; Tinker, L. L. The Path to Perovskite Commercialization: A Perspective from the United States Solar Energy Technologies Office. *ACS Energy Lett.* **2022**, 1728–1734. <https://doi.org/10.1021/acsenenergylett.2c00698>.
- (4) Aristidou, N.; Sanchez-Molina, I.; Chotchuangchutchaval, T.; Brown, M.; Martinez, L.; Rath, T.; Haque, S. A. The Role of Oxygen in the Degradation of Methylammonium Lead Trihalide Perovskite Photoactive Layers. *Angew. Chem. Int. Ed.* **2015**, *54* (28), 8208–8212. <https://doi.org/10.1002/anie.201503153>.
- (5) Kim, Y.; Yang, Z.; Jain, A.; Voznyy, O.; Kim, G.-H.; Liu, M.; Quan, L. N.; Garcia de Arquer, F. P.; Comin, R.; Fan, J. Z.; Sargent, E. H. Pure Cubic-Phase Hybrid Iodobismuthates AgBi₂I₇ for Thin-Film Photovoltaics. *Angew. Chem. Int. Ed.* **2016**, *55* (33), 9586–9590. <https://doi.org/10.1002/anie.201603608>.
- (6) Pai, N.; Lu, J.; Gengenbach, T. R.; Seeber, A.; Chesman, A. S. R.; Jiang, L.; Senevirathna, D. C.; Andrews, P. C.; Bach, U.; Cheng, Y.-B.; Simonov, A. N. Silver Bismuth Sulfoiodide Solar Cells: Tuning Optoelectronic Properties by Sulfide Modification for Enhanced Photovoltaic Performance. *Adv. Energy Mater.* **2019**, *9* (5), 1803396. <https://doi.org/10.1002/aenm.201803396>.
- (7) Traoré, B.; Basera, P.; Ramadan, A. J.; Snaith, H. J.; Katan, C.; Even, J. A Theoretical Framework for Microscopic Surface and Interface Dipoles, Work Functions, and Valence Band Alignments in 2D and 3D Halide Perovskite Heterostructures. *ACS Energy Lett.* **2021**. <https://doi.org/10.1021/acsenenergylett.1c02459>.
- (8) Cucco, B.; Pedesseau, L.; Katan, C.; Even, J.; Kepenekian, M.; Volonakis, G. Silver-Bismuth Halide Double Salts for Lead-Free Photovoltaics: Insights From Symmetry-Based Modeling Supporting Information.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Room temperature synthesis of green emitting lead-free perovskite inspired manganese halides

Pierre MARTIN, Audrey POTDEVIN, Geneviève CHADEYRON, Damien BOYER

¹Université Clermont Auvergne, Clermont Auvergne INP, CNRS, Institut de Chimie de Clermont-Ferrand, Clermont-Ferrand, France.

Type of communication: Oral

Inorganic lead halide perovskites, with a general formula CsPbX_3 ($X=\text{Cl}^-, \text{Br}^-, \text{I}^-$) have triggered a huge scientific interest, particularly since 2015. Even if they show excellent quantum yields, narrow and tunable emission band, their poor stability against oxygen, moisture, thermal and photonic stresses needs to be considered for application in LED devices. Moreover, lead (Pb) amount in electronic compounds is restricted to 1000 ppm by the RoHS, considering the risk for human health. Consequently, to overcome this major drawback, the development of stable and Pb free halides is currently attracting strong interest [1].

Herein, we employed a rapid and room-temperature synthesis to achieve Cs_3MnBr_5 micron-sized crystals (Figure 1 A). Its strong green emission upon blue or UV excitation (Figure 1 B and C) is attributed to manganese (II) ${}^4T_1 \rightarrow {}^6A_1$ transition, partially allowed in tetrahedral environment. A better air stability was achieved through zinc alloying, which was correlated with a slower hydration kinetics. We show that an increase in x value in $\text{Cs}_3\text{Mn}_x\text{Zn}_{1-x}\text{Br}_5$ improved blue light absorption, but is also responsible for an internal quantum yield drop, which has been correlated with a concentration quenching phenomenon and with a worst crystallinity.

Through this work, we developed a narrow band (FWHM~40nm) green-emitting halide ($\lambda_{em} = 520\text{nm}$) with high internal quantum yield (~60%), which is particularly promising for an association with (micro)-LED.

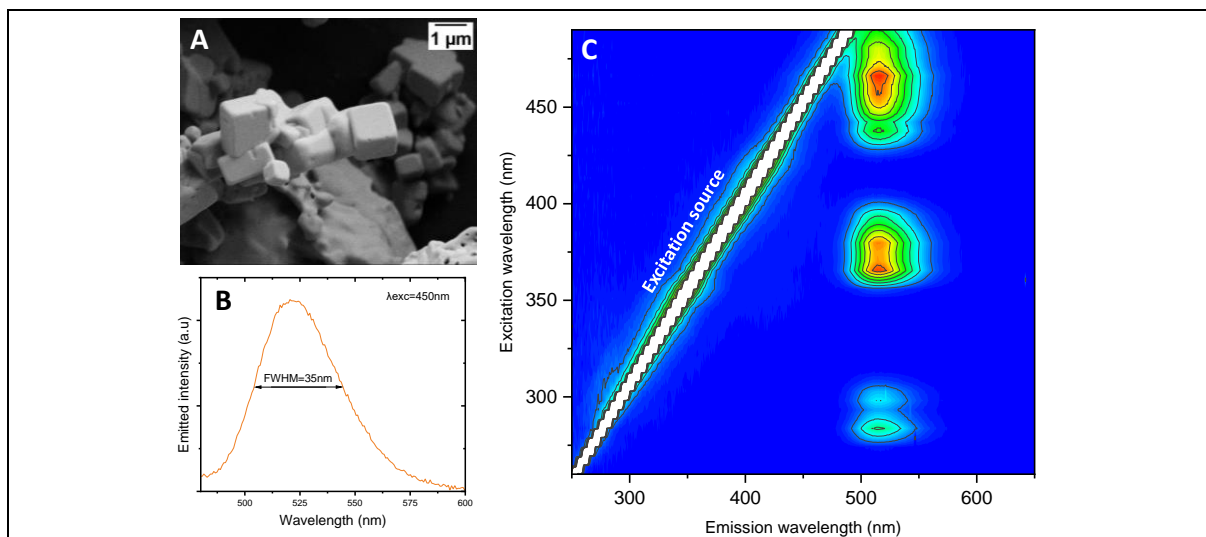


Figure 1. SEM picture (A), emission spectra under blue (450nm excitation) excitation (B) and excitation-emission map (C) of $\text{Cs}_3\text{Zn}_{0.5}\text{Mn}_{0.5}\text{Br}_5$.

References

- [1] A. Dey *et al.*, « State of the Art and Prospects for Halide Perovskite Nanocrystals », *ACS Nano*, vol. 15, n° 7, p. 10775-10981, juill. 2021, DOI: 10.1021/acsnano.0c08903.

Acknowledgements

This work was supported by the International Research Center "Innovation, Transportation and Production Systems" of the I-site CAP20-25.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Long-range and ballistic propagation at room temperature of 75% excitonic fraction polaritons in perovskite metasurface.

N.H.M. Dang¹, S.Zanotti², C. Chevalier¹, E. Drouard¹, G. Trippé-Allard³, E. Deleporte³, D. Gerace², C. Seassal¹, [H. S. Nguyen](#)^{1,4}

1. Univ Lyon, Ecole Centrale de Lyon, INSA Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, INL, UMR5270, Ecully 69130, France
2. Dipartimento di Fisica, Università di Pavia, via Bassi 6, I-27100 Pavia, Italy
3. Lumière, Matière et Interfaces (LuMI) Laboratory, Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupélec, 91190 Gif-sur-Yvette, France

Type of communication: Oral

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 their 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 propagation at room temperature in resonant metasurfaces made from a sub-wavelength two-dimensional lattice of perovskite pillars that are fabricated by thermal nano-imprint [2]. Room temperature polaritons are demonstrated with a remarkable Rabi splitting in the 200 meV range. In particular, the experiment revealed a ballistic propagation distance of polaritons over hundreds of micrometers at room temperature even with large excitonic component up to 75% [3]. This long-range propagation is enabled by the high homogeneity of the metasurface, and by the large Rabi splitting which completely decouples polaritons from the phonon bath at the excitonic energy. Our 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.

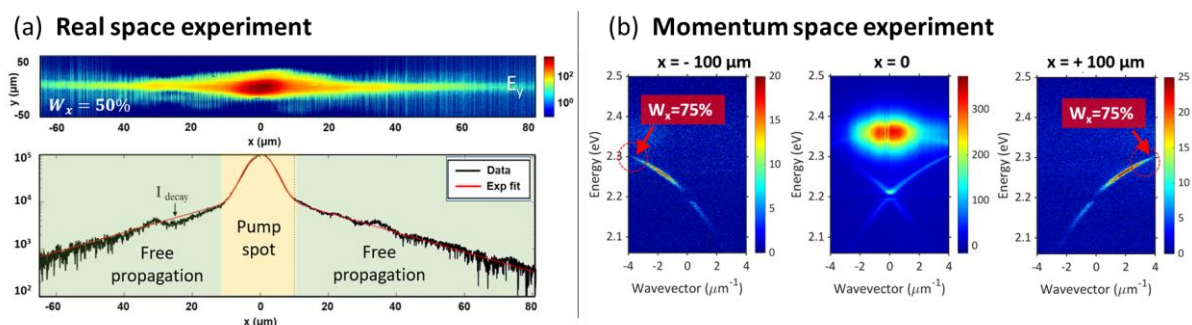


Figure 1. (a) Spatially resolved photoluminescence corresponding to excitonic fraction 50%. (b) Angular resolved photoluminescence measured at different propagation position. The propagation at 100 μm away from the pump spot shows no back scattering, and polaritons of 75% excitonic fraction are observed.

References

- [1] C. Weisbuch et al, Phys. Rev. Lett. 69, 3314 (1992).
- [2] R. Mermet Lyaudoz et al, arXiv:2212.10122
- [3] N.H.M. Dang et al, in preparation



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Deep-learning assisted identification of new hybrid perovskites from X-ray diffraction patterns

Romain Gautier,¹ Florian Massuyeau,¹ Thibault Broux,¹ Florent Coulet,¹ Aude Demessence,² Adel Mesbah²

¹ Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes, F-44000 France

² Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, Villeurbanne, F-69626 France

Type of communication: Oral

Hybrid lead halides of perovskite type have recently shown a great potential in optoelectronic applications. For this reason, many research groups are currently exploring this chemical system to discover new low dimensional hybrid perovskites. However, discovering such materials is challenging as the necessary structure determination by X-ray crystallography is time consuming and non-perovskite compounds are very often synthesized instead of perovskites.

In this context, we developed a deep learning approach, which automatically and accurately assign the structure type from the X-ray diffraction patterns of new hybrid lead halides. We were able to identify and explain the key features in the diffraction patterns, which allow the machine learning algorithms to discriminate between perovskites and non perovskites. From this information, the scientists' ability in discriminating the different structure types can be augmented.

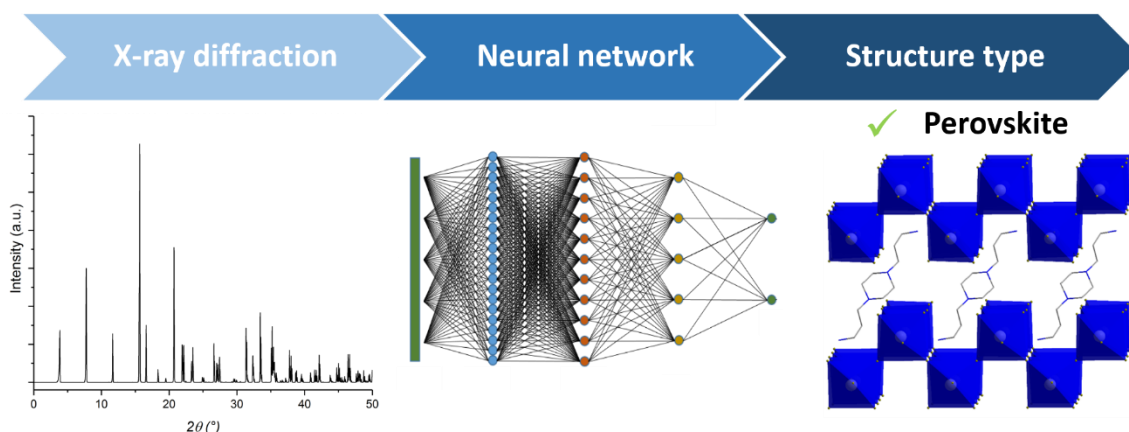


Figure 1. From the powder X-ray diffraction pattern of a new hybrid lead halide materials to the information of its structure type using deep learning.

References

[1] F. Massuyeau, T. Broux, F. Coulet, A. Demessence, A. Mesbah, R. Gautier, **Advanced Materials**, (2022) 34(41)



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Donor-Acceptor Pair Transitions in Halide Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ Single Crystals

¹Joanna M. Urban*, ³[Thi Huyen Trang Nguyen](#), ¹Gabriel Chehade, ³Aymeric Delteil, ¹Gaëlle Allard-Trippé, ²Geraud Delport, ¹Emmanuelle Deleporte, ³Jean-Pierre Hermier, ³Damien Garrot

¹Université Paris-Saclay, ENS Paris-Saclay, Centrale Supélec, CNRS, LuMIn, F-91190 Gif-sur-Yvette, France

²CNRS, UMR 9006, IPVF, Institute Photovoltaïque d'Île-de-France, 18 Boulevard Thomas Gobert, Palaiseau 91120, France

³Université Paris-Saclay, UVSQ, CNRS, GEMaC, 78000, Versailles, France

* Currently at Fritz Haber Institute of Max Planck Society, 14195 Berlin, Germany

Type of communication: Oral

A better understanding of the defect physics in halide perovskites is a crucial challenge to improve further the efficiency of perovskite solar cells. [1] Here, the defect emission of Methylammonium lead iodine (MAPbI_3) single crystals is investigated systematically based on the steady-state and time-resolved photoluminescence spectroscopy (TRPL) at cryogenic temperature. We observe the emission of Donor-acceptor pair (DAP) recombination due to the presence of native shallow defects. The spectral characteristics of DAP recombination present an important variability depending on the local position on the crystal, due to an inhomogeneous defect distribution. A strong blueshift of the emission as a function of power is explained by the existence of potential fluctuation induced by compensated defects. With increasing excitation power, a transition is observed between a structureless and structured DAP band with several longitudinal-optical phonon (LO-phonon) replicas. The DAP transitions are characterized by non-exponential photoluminescence decays and the redshift of the emission with time. Based on measurements on the pristine surface of cleaved crystals, series of sharp lines with sub-meV widths, the characteristic spectral signature of discrete DAP recombination, are resolved.

References:

- [1] Ball, J. M. and Petrozza, A., Nature Energy 2016 1(11).
- [2] J. Kim, S.-H. Lee, J. H. Lee, K.-H. Hong, The Journal of Physical Chemistry Letters 2014, 5, 8 1312.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Tight-binding modelling of layered halide perovskites

[Simon Thébaud](#)¹, Bruno Cucco², Claudio Quarti³, Georges Volonakis², Laurent Pedesseau¹,

Mikael Kepenekian², Claudine Katan², Jacky Even¹

¹*Univ Rennes, INSA Rennes, CNRS, Institut FOTON – UMR 6082, France*

²*Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes – UMR 6226, France*

³*Univ Mons, FNRS, Laboratory for Chemistry of Novel Materials, Belgium*

Type of communication: Oral

In recent years, layered heterostructures of halide perovskites have emerged as promising optoelectronic systems due to their tunability and to the presence of strong excitonic effects [1], with potential applications for efficient light emission, spintronics, single-photon emission and photonic logic. This last technology is being developed by the H2020 POLLOC (polariton logic) consortium using exciton-polariton devices. From the theoretical point of view, first-principles studies of exciton physics in layered halide perovskites are possible [2] but severely constrained by system size. To go beyond this limitation, symmetry-based semi-empirical tight-binding models have provided an efficient description of the electronic structure and optical properties of bulk halide perovskites [3-5]. In this talk, we will discuss such models and their extension to the case of layered perovskites, a stepping stone towards a robust description of excitons in these compounds within the tight-binding framework [6,7].

References

- [1] J.-C. Blancon et al., *Nature Comm.* 9, 2254 (2018)
- [2] C. Quarti et al., *Adv. Optical Mater.* 2023, 2202801
- [3] S. Boyer-Richard et al., *J. Phys. Chem. Lett.* 7, 3833 (2016)
- [4] A. Marronnier et al., *ACS Nano* 12, 3477 (2018)
- [5] Z. Wei et al., *Nature Comm.* 10, 5342 (2019)
- [6] R. Benchamekh et al., *Phys. Rev. B* 91, 045118 (2015)
- [7] Y. Cho et al., *Phys. Chem. Lett.* 10, 6189 (2019)



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Detailed Analysis and Modelling of the Photocurrent Response of $\text{MAPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ Single Crystals under X-rays

Ferdinand Lédée^a, Javier Mayén Guillén^b, Oriane Baussens^a, Marian Chapran^a, Thibault Lemerrier^c, Jean-Marie Verilhac^b, Eric Gros Daillon^a, Alain Ibanez^c, Julien Zaccaro^c

^a Grenoble Alpes University, CEA, LETI, DOPT, F38000 Grenoble, France

^b Grenoble Alpes University, CEA, LITEN, DTNM, F38000 Grenoble, France

^c Grenoble Alpes University, CNRS, Grenoble INP, Institut Néel, F38042 Grenoble, France

Type of communication : Oral

Halide perovskites have been revealed as compulsory materials in the research field of optoelectronics, with device performances matching the state-of-the-art for UV-Visible photodetection and X- and Gamma-rays detection. In this picture, the analysis of the photocurrent response under irradiation is paramount, as it is used to both characterize the performances of the devices as well as investigating the fundamental properties of the perovskite material. More specifically, the photocurrent carries information on the transport of the photogenerated charge carriers, and thus can be modeled in specific conditions by the so-called Hecht equation to quantify the free charge mobility μ and lifetime τ product. Consequently, the photocurrent is widely employed as a proxy to assess the overall quality of the material in terms of transport. Yet, the hypothesis associated to the Hecht equation are often overlooked, which can possibly lead to misinterpretation of the results.

In this work, we will provide a thorough analysis of the photocurrent response under medical X-rays for a model material, namely $\text{MAPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ single crystals. The physical mechanism responsible for the photocurrent will be carefully examined, and the relevancy of one of the hypothesis for the modelling of the photocurrent (uniformity of the electric field) will be specifically discussed.[1] Finally, the benefits of Cl-alloying in $\text{MAPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ perovskites for the charge transport will be demonstrated.[2] We believe that a more rigorous analysis of the photocurrent response will help the development of UV-Visible photodetectors and radiation detectors, and may provide a powerful tool for the material science research applied to halide perovskites if used in the right conditions.

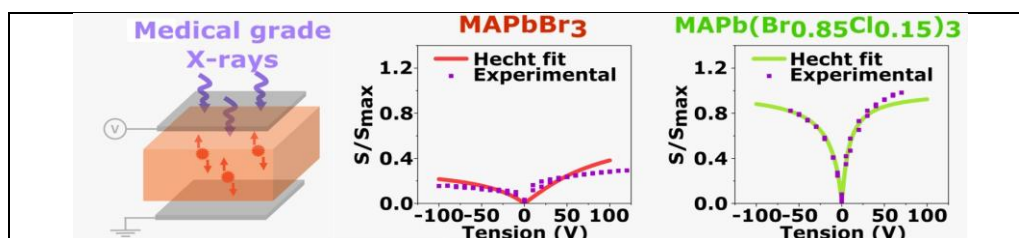


Figure 1. Response under X-rays of $\text{MAPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ single crystals (0% and 15% Cl-content respectively)

References

- [1] O. Baussens *et al.*, « An insight into the charge carriers transport properties and electric field distribution of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thick single crystals », *Appl. Phys. Lett.*, vol. 117, n° 4, p. 041904, July 2020, doi: 10.1063/5.0011713.
- [2] J. Mayén Guillén *et al.*, « $\text{MAPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ hybrid perovskite materials for direct X-ray detection », *ACS Applied Electronic Materials*, **Accepted**.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Elaboration of new hybrid perovskite@graphite composites and mixed 2D/3D perovskites with enhanced stability for X-ray detection via a solvent-free mechanochemical approach

Yihui Cai¹, D. Begin¹, C. Sidhoum², A. Girault², D. Preziosi², C. Lefevre², F. Ledee³, E. Gros D'Aillon³, M. Gallart², P. Gilliot², O. Ersen², C. Sanchez⁴, S. Begin-Colin²

1. *Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), UMR-7515 CNRS, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, France*
2. *Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR-7504 CNRS, Université de Strasbourg, 23 rue du Lœss, 67034 Strasbourg Cedex 2, France*
3. *CEA-Leti, 17 avenue de Martyrs, 38054 Grenoble, France*
4. *Sorbonne Université, CNRS UMR 7574, Collège de France, LCMCP, 4 place Jussieu & USIAS Strasbourg, France*

Type of communication: Oral

In the last few years, hybrid perovskites (HP) have emerged as a new class of semiconductors with outstanding performance, becoming a key player in optoelectronic, in particular, as X-ray detectors, exhibiting relatively high charge mobility, long carrier recombination lifetime, large X-ray attenuation coefficient and tunable bandgap. However, their industrial development is hampered because of their chemical (air) and thermal instabilities. Recently, a new solvent-free method, the mechanosynthesis, has emerged as a powerful alternative for the HPs synthesis to easily produce high-performance HP with a better stability in large quantity. We have successfully mechanosynthesized (MS) a commonly studied 3D hybrid perovskite: methylammonium lead iodide (MAPbI₃) and optimized the synthesis parameters. We have thus combined HP with graphite by mechanosynthesis as graphite may protect HP from moisture due to its hydrophobicity. HP@graphite composites with different amounts of graphite were elaborated. Both steady-state and time-resolved photoluminescence spectra as a function of graphite content illustrated that strong interactions between graphite and HP occurred. Moreover, the InSitu high-resolution TEM highlighted the common crystallographic orientations between nanograins (~10nm) in aggregates of MS powders. Another strategy to further enhance the HP stability is to combine the outstanding optoelectronic properties of the 3D HPs with the high environmental robustness of the layered 2D phase (obtained with "larger" ammonium molecule). We have successfully inserted the 3D phase into the layered 2D structure through a one-pot mechanochemical approach, studying the effect of the ammonium chain nature driving the 2D phase for the X-ray detector performance.



Résumés des posters (dans l'ordre alphabétique par auteur.ice)
/ *Posters abstracts* (*in alphabetical order in author's name*)



Liste des 23 posters (par ordre alphabétique de l'auteur.ice)
/ List of the 23 posters (in alphabetical order of the author)

- P1.** “Contribution of Grazing Incidence Fast Atom Diffraction (GIFAD) to the growth of MAPbI₃”
ALLOUCHE Abdel Rahman – ISMO
- P2.** “Digital printing of SnO₂ Electron Transporting Layer for air processed perovskite Solar Cells”
BOUZID Hamza – Institut Galilée
- P3.** “Tetraphenylpyrrolo[3,2-b]pyrroles: Synthesis, Thermal, Optical, Electrochemical Properties and Photovoltaic Applications”
BUI Thanh-Tuân – LPPI
- P4.** “Polymorphous hybrid perovskites showing different photoluminescence properties”
CAZALS Clémence – MOLTECH-Anjou
- P5.** “Raman Spectroscopic Studies of Cs₂B'B''X₆ Lead-Free Halide Double Perovskites”
CHOLASETTYHALLI DAKSHINAMURTHY Athrey – IIT Madras
- P6.** “Defect production and positron annihilation at vacancies in lead iodide perovskite layers”
CORBEL Catherine – LSI Ecole Polytechnique
- P7.** “ALD of niobium oxide (Nb₂O₅) and niobium-doped titanium oxide (Nb:TiO₂) for solar cell applications”
COUTANCIER Damien – IPVF CNRS
- P8.** “Photoluminescence and Ellipsometry spectroscopies embedded in a ALD platform to control and analyze perovskites thin film and interfaces”
DELPORT Géraud – IPVF CNRS
- P9.** “Copper-doped nickel oxide for inverted perovskite solar cells: Impact of Cu-doping and annealing temperature on PV cell parameters”
DRIDI REZGUI Béchir – CRTEN Tunis
- P10.** “Synthesis of bismuth halide perovskite nanocrystals for photoelectrocatalytic CO₂ reduction”
GHOSH Antik – CEA Grenoble
- P11.** “A theoretical framework to examine and tailor electronic and optoelectronic properties of halide double perovskites”
GUPTA Mayank – IIT Madras
- P12.** “Introduction of phosphonic acid-based molecules as Self-Assembled Monolayers for MAPbI₃ perovskite solar cells”
HAMI Yahya – ITODYS



- P13.** “Fabrication of All-Inorganic Perovskite CsPbBr₃ Thick Films using Close Space Sublimation”
Jakob IHRENBERGER – CEA Grenoble
- P14.** “Amino-terminated SAMS for the functionalization of mp-TiO₂ in Hybrid Perovskite Solar Cells”
LANG Philippe – ITODYS
- P15.** “On the necessity of similarity between the terminal function of an amino SAMs with the cation of the hybrid perovskite in a PV cell: advantage of a mono-oriented ZnO layer”
LANG Philippe – ITODYS
- P16.** “Solution Grown Thick Polycrystalline Halide Perovskite Monoliths for X-ray Detection”
LEMERCIER Thibault – CNRS Institut Néel
- P17.** “Multi-resonances for simultaneous enhancement of two-photon absorption and photoluminescence extraction in perovskite metasurface”
NGUYEN Trong Tam – Ecole Centrale de Lyon
- P18.** “First integration of amorphous carbon nitride layers in electrodeposited perovskite solar cells”
PAILLERET Alain - LISE
- P19.** “Synthesis of inorganic halide perovskite targets for pulsed laser thin film deposition”
PARRAT Elsa – CEA Leti
- P20.** “Using Hansen solubility parameters to understand solvent-antisolvent interactions in metal halide perovskites”
PAULUS Fabian - Leibniz-Institute for Solid State and Materials Research IFW
- P21.** “Band-Edge Exciton Fine Structure and charge-carrier interactions in Lead-Halide Perovskite Nanocrystals”
PRIN Elise – LP2N
- P22.** “Modification of the light emission properties of individual inorganic perovskite nanocrystals using a versatile photonic structure”
SAID Zakaria – LPENS
- P23.** “Tin iodide perovskites with methylammonium activated by Self-Assembled Monolayers for solar cell efficiency and stability”
SLIMI Bechir – ITODYS



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Contribution of Grazing Incidence Fast Atom Diffraction (GIFAD) to the growth of MAPbI_3

A. R. Allouche^{1,2}, E. M. Staicu Casagrande¹, A. Momeni¹, A. Ouvrard¹, G. Trippé-Allard³, D. Garrot⁴, E. Deleporte³, H. Khemliche¹

¹ ISMO, Université Paris-Saclay, CNRS, 91405, Orsay, France

² LPM, Laboratoire de Physique et Modélisation, EDST, Lebanese University, 1300 Tripoli, Lebanon

³ LUMIN, Université Paris-Saclay, ENS Paris -Saclay, CentraleSupélec, CNRS, 91190 Gif-sur-Yvette, France

⁴ GEMAC, Université Paris-Saclay, UVSQ, CNRS, 78000, Versailles, France

Corresponding author: abdel-rahman.allouche@universite-paris-saclay.fr

Hybrid perovskite thin films have gathered significant attention in recent years owing to their special optoelectronic properties. However, their application on a large scale is limited by several issues, including (i) their degradation caused by environmental interactions (light, humidity, etc.), (ii) their interactions and dynamics at the interfaces (charge transport layers, electrodes, etc.) and (iii) the difficulty of producing high quality layers on a large area. Deposition by vacuum evaporation may contribute to solve some of the issues mentioned above¹. Although this method indeed offers a better control of the layer quality and thickness, the growth process inherently produces a PbI_2 rich interface with the substrate², which increases the recombination rate³. The challenge then consists in developing a method that allows a more complete control of the interface and the subsequent growing layers on the atomic scale.

Grazing Incidence Fast Atom Diffraction (GIFAD), a novel characterization technique that exploits the quantum scattering of He atoms at keV energies, enables real-time characterization of a growing layer⁴. GIFAD provides a direct information on the organization dynamics by resolving the evolution of electron density profile of the very top layer⁵. The latter can then be related to atomic positions within the unit cell. Because GIFAD is absolutely non-destructive, it is possible to monitor the growth of very fragile materials, such as MAPbI_3 , over long periods.

Figure 1 shows the time evolution of the diffraction pattern (top panel) when the MAPbI_3 components are deposited sequentially on Ag (100). Starting with an initial $\text{CH}_3\text{NH}_3\text{I}$ (MAI) monolayer (with a square lattice), further deposition of both PbI_2 and MAI produces a sharp transition to a new square crystalline structure that eventually evolves to a PbI_2 rich hexagonal lattice. Evolution of the relative intensities of the diffraction peaks (bottom panel) reveals that the fading structure, beyond the sharp transition, is not simply being covered by a PbI_2 hexagonal layer. Rather, it continuously evolves with time through changes in its atomic positions; this dynamics should provide valuable information of the building-up of the MAPbI_3 layer. A more complete analysis, gained through a multi-technique approach, will be provided at the conference.

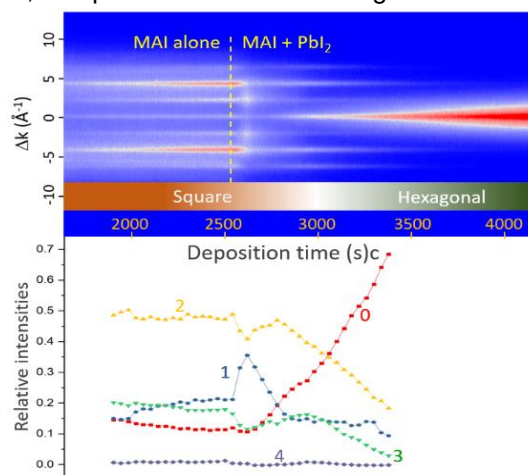


Fig. 1. Time evolution of the GIFAD pattern as MAI+ PbI_2 co-deposition (shown by the vertical dashed line) follows the deposition of a pure MAI monolayer on Ag (100).

¹ Liu, M., Johnston, M. & Snaith, Nature 501, 395 (2013). <https://doi.org/10.1038/nature12509>

² Haitao Xu et al., Organic Electronics 69, 329 (2019). <https://doi.org/10.1016/j.orgel.2019.03.047>

³ Haitao Xu et al., Phys. Chem. Chem. Phys. 18, 18607 (2016). <https://doi.org/10.1039/C6CP02737G>

⁴ P. Atkinson et al.; Appl. Phys. Lett. 105, 021602 (2014) <https://doi.org/10.1103/PhysRevB.90.155308>

⁵ H. Khemliche et al.; Appl. Phys. Lett. 95, 151901 (2009) <https://doi.org/10.1063/1.3246162>



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Digital printing of SnO₂ Electron Transporting Layer for air processed perovskite Solar Cells

Hamza Bouzid,^{1, 2,*} Sylvain Vedraïne¹, Abdelaziz Bouazizi,² Mahfoudh Raissi,³ Johann Bouclé,¹

¹ Univ. Limoges, XLIM, UMR 7252, F-8700 Limoges, France

² Univ. Monastir, LMCN Monastir, Tunisie

³ KELENN TECHNOLOGY, 4, Avenue François Arago 92160 Antony - France

hamza.bouzid91@gmail.com

sylvain.vedraine@xlim.fr

Type of communication: **Oral**

DMD 100 printing is a digital deposition technique, rapid and scalable that allows for processing of high quality thin films without material waste, as required for the commercialization of solar cells. Herein, this technique was used to prepare compact SnO₂ films. Through the ink formulation and the adjustment of the printing parameters, a homogenous SnO₂ layer was obtained, and then inserted into perovskite solar cells to act as an electron transporting layer (ETLs). Triple cation perovskite solar cells were fabricated in ambient conditions. The efficiency of the SnO₂-printed devices were measured and compared to the reference SnO₂-spin coating devices. SnO₂-printed based devices yields a high efficiency of 17,3% with a long term air stability, outperforming the reference devices. This work contributes to highlight the scale-up of thin film using digital printing techniques for the next generation photovoltaic applications.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Tetraphenylpyrrolo[3,2-*b*]pyrroles: Synthesis, Thermal, Optical, Electrochemical Properties and Photovoltaic Applications.

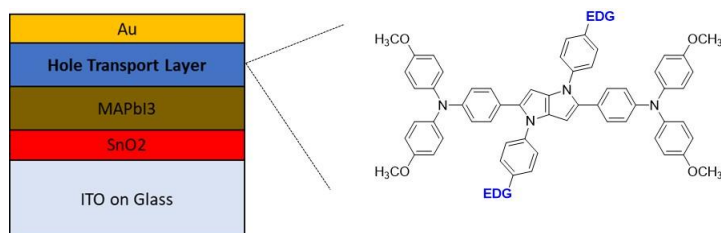
Thanh-Tung Dang,¹ Michael Spence,² Suzanne K. Thomas,² Matthew Carnie,² **Thanh-Tuân Bui**^{1*}

¹CY Cergy Paris Université, LPPI, F-95000 Cergy, France.

²Department of Materials Science & Engineering, and SPECIFIC-IKC, Swansea University, Bay Campus, Fabian Way, Swansea SA1 8EN

Corresponding author: T T Bui (tbui@cyu.fr)

Type of communication: Poster



We reported two tetraphenylpyrrolo[3,2-*b*]pyrroles in which the central core is functionalized by electron-rich functions: methoxy and di(4-methoxyphenyl)aminy. The targeted compounds have good solubility in common organic solvents, high thermal stability and glass forming capacity. The optical and electrochemical properties of these compounds suggest use in a diverse range of applications. When utilized as the hole transporting layer of the planar perovskite solar cells, power conversion efficiencies ranging from 12.8 to 14.5% were obtained.

Reference:

1. T.-T. Dang, M. Spence, S. K. Thomas, M. Carnie, **T.-T. Bui**, *Journal of Materials Science: Materials in Electronics* **2022**, 33, 17773 – 17779.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

POLYMORPHOUS HYBRID PEROVSKITES SHOWING DIFFERENT PHOTOLUMINESCENCE PROPERTIES

Clémence CAZALS,¹ Nicolas Mercier,¹ Romain GAUTIER ² and Florian Massuyeau ²

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

clemence.cazals@univ-angers.fr, <https://moltech-anjou.univ-angers.fr/fr/index.html>

² IMN, Nantes University, Nantes, France

Type of communication: Poster

Abstract: Hybrid perovskites have been more and more studied because of their white emission property making them promising materials for optoelectronics applications. ^[1-2] Here two polymorphs of the hybrid perovskite (C3a)₂PbBr₄ (C3a = HO₂C(CH₂)₂NH₃⁺), stable at room temperature, which shows different photoluminescence properties has been successfully synthesized by precipitation method. Indeed, two phases were obtained: the thermodynamically stable phase α -(C3a)₂PbBr₄ and the metastable phase β -(C3a)₂PbBr₄. As revealed by Differential Scanning Calorimetry (DSC), the β -phase can be obtained by heating the α -phase at 110°C, while the reversibility is not observed upon cooling to RT. However, it has been observed that the β -phase goes back to the α -phase either thanks to the humidity or by grinding. α -(C3a)₂PbBr₄ has a broad band white emission (with a major blue contribution at 439 nm) and β -(C3a)₂PbBr₄ has a blue photoluminescence at 424 nm (Fig. 1). We show that the 6s₂ lone pair stereo activity may have a key role in the broad band emission of the alpha phase. Moreover, this perovskite has a congruent melting property. This opens new opportunities to design and tune the properties of these materials.

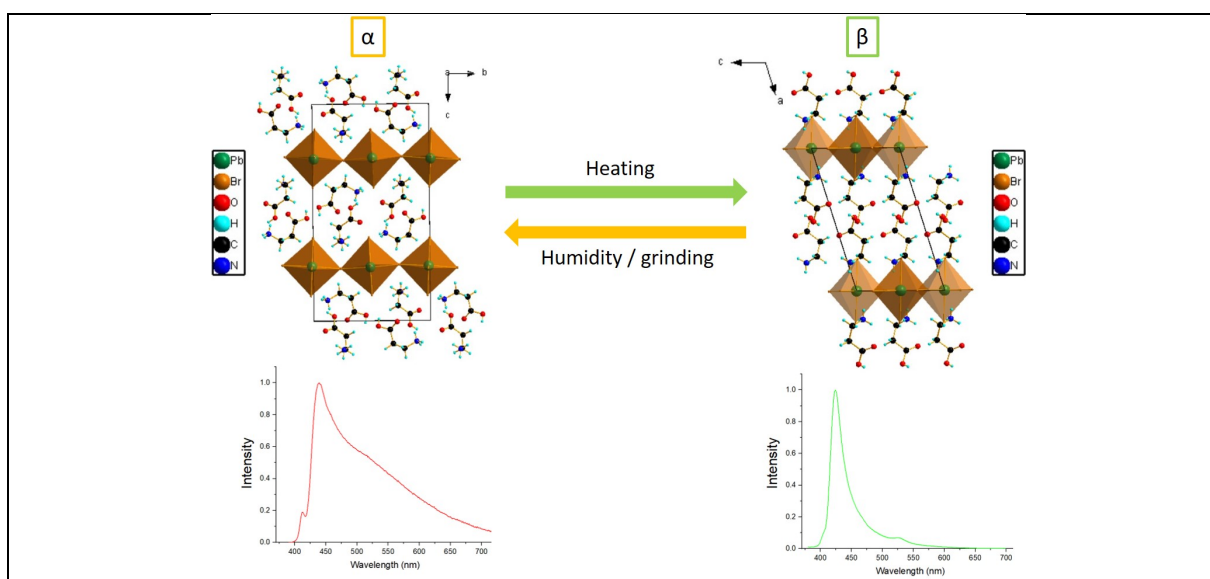


Figure 1. α -(C3a)₂PbBr₄ (on the left) and β -(C3a)₂PbBr₄ (on the right) structures and corresponding PL spectra. The green arrow indicates the phase transition from α -phase to β -phase. The yellow arrow indicates the reversibility phenomenon.



JPH 2023

Journées Perovskites Halogénées

31/05 - 02/06 Biarritz, France

References

- [1] Feten Hleli, F; Mercier, N; Ben Haj Salah, M; Allain, M; Travers, T; Gindre, D; Zouarib, N; Botta, C, J. Mater. Chem. C. 2022, 10 (28), 10284-10291
- [2] Matthew D. Smith; Hemamala I. Karunadasa; Accounts of Chemical Research. 2018, 51 (3), 619-627



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Raman Spectroscopic Studies of $\text{Cs}_2\text{B}'\text{B}''\text{X}_6$ Lead-Free Halide Double Perovskites

Athrey C Dakshinamurthy and C Sudakar

*Multifunctional Materials Laboratory, Department of Physics, Indian Institute of Technology
Madras, Chennai, India*

Type of communication: Oral

Abstract: Vibrational dynamics in halide double perovskites govern several key aspects including carrier recombination and transport properties. Here we present a comprehensive vibrational studies on lead-free halide double perovskites $\text{Cs}_2\text{B}'\text{B}''\text{Cl}_6$ ($\text{B}' = \text{Ag}_{1-x}\text{Na}_x$; $\text{B}'' = \text{Bi}_{1-x}\text{In}_x$; $\text{X} = \text{Cl, Br}$) investigated through micro-Raman spectroscopy to understand various atomic contributions to the lattice vibrations. The vibrational dynamics differ largely between cationic substitution and anionic substitution. A significant enhancement in cationic ordering is observed with Na^+ substitution at B' site while alloying at the B'' site shows distinct vibrational modes arising from the cation substituted octahedra. On the other hand, Raman studies of the halogen substitution in these double perovskites, conventionally assumed to exhibit homogeneous mixing of anions, reveal that such a generalization can be significantly misleading. Our results show that metal-halide octahedra are either Cl or Br rich in anionic alloyed double perovskites. An equal number of dissimilar halogen atoms in each octahedron as conventionally assumed to exist is not a stable configuration. The changes in the vibrational mode intensities with B' site substitution (Ag^+ , Na^+) and the appearance of distinct octahedral modes with B'' site substitution (Bi^{3+} , In^{3+}) allows us to disseminate the different octahedral contributions to the vibrational dynamics in the lattice. This renewed fundamental understanding on the miscibility of atomic substitution will open up scopes and the necessities to revisit the mechanisms of stability and optoelectronic properties. The vibrational analyses on double perovskites with different choices of B' and B'' cations and X anion reveal the origin of asymmetric stretching (E_g) modes. This mode mainly prevails when sublattice distortions in the lattice exist. Thus, asymmetric stretching mode can be a measure of sublattice distortion in the double perovskite and a highly ordered system would exhibit very minimal or no asymmetric vibrations.

References

- [1] *J. Phys. Chem. C* 2023, 127, 3, 1588–1597; <https://doi.org/10.1021/acs.jpcc.2c05806>
[2] *Appl. Phys. Lett.* **118**, 131902 (2021); <https://doi.org/10.1063/5.0046423>



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Defect Production and Positron Annihilation at Vacancies in Lead Iodide Perovskite Layers

P. Aversa¹, M. Kim², V. Léger^{1*}, H. Lee², D. Tondelier², O. Plantevin³, J. Botsoa⁴, P. Desgardin⁴, J.E Bourée², L. Liskay⁵, M. Dickmann⁶, W. Egger⁶, M.F. Barthe⁴, D. Ceratti^{7,**}, F. Oswald⁸, B. Geffroy^{2,8}, C. Corbel¹

¹ LSI, CEA/DRF/IRAMIS, CNRS, Ecole polytechnique, Institut Polytechnique de Paris, 91128 Palaiseau, France

² LPICM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, 91128 Palaiseau, France

³ LPS, 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 Institut Photovoltaïque d'Île de France (IPVF), CNRS, 18 Boulevard Thomas Gobert, 91120 Palaiseau, France y

⁸ Université Paris-Saclay, CEA, CNRS, NIMBE, LICSEN, 91191 Gif-sur-Yvette, France

Present Address: *C2N, CNRS, Université Paris-Saclay, 91120 Palaiseau, France ; **Sorbonne Université, CNRS, Collège de France, Chimie de la Matière Condensée de Paris, 75005 Paris, France

Type of communication: Oral

Hybrid organic-inorganic lead halide perovskites (HOIPs) attract much attention for their application in optoelectronic devices. However, the long-term stability remains one of the major concerns for the large-scale utilization of the perovskite technology [1,2]. Ion migration has been shown to be at origin of hysteresis in lead halide perovskites [3,4] and to play a dominant role at the interfaces [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 near the interfaces-

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_xBr_{1-x})₃ layers spin-coated on substrates. An intriguing property is the lack of response of the annihilation fingerprints to the production of defects in such layers after high energy ion or electron beam irradiation. The annihilation characteristics, e⁻_e⁺ annihilating pair momentum distribution, are consistent with annihilation fingerprints arising from capture at huge native vacancy concentration, $\geq 3 \cdot 10^{18} \text{cm}^{-3}$, that efficiently capture thermalized positrons before their annihilation in pristine as well as irradiated layers. The nature of the dominant vacancies capturing positrons is discussed [6].

REFERENCES

- [1] Fu et al., Recent progress on the long-term stability of perovskite solar cells. *Adv. Sci.* 5, 1700387 (2018).
- [2] Wang et al. A Review of Perovskites Solar Cell Stability. *Adv. Funct. Mater.* **2019**, 1808843
- [3] Miyano et al., Hysteresis, Stability and Ion Migration in Lead Halide Perovskite Photovoltaics. *J. Phys. Chem. Lett.* **2016**, 7, 2240
- [4] Lee et al., Direct Experimental Evidence of Halide Ionic Migration under Bias in CH₃NH₃PbI_{3-x}Cl_x Based Perovskite Solar Cells using GD-OES Analysis. *ACS Energy Lett.*, **2017**, 2, 943.
- [5] Kim et al., Halide Ion Migration and its Role at the Interfaces in Perovskite Solar Cells. *Eur. J. Inorg. Chem.* **2021**, 46, 4781
- [6] Dhar et al. Investigation of Ion-Mediated Charge Transport in Methylammonium Lead Iodide Perovskite. *J. Phys. Chem. C* **2017**, 121, 5515



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

ALD of niobium oxide (Nb₂O₅) and niobium-doped titanium oxide (Nb:TiO₂) for solar cell applications

Thomas Vincent,^a Damien Coutancier,^{a,b} Pia Dally,^{a,c} Mirella Al-Katrib,^{a,c} Frédérique Donsanti,^{a,d} Armelle Yaïche,^{a,d} Karim Medjoubi,^a Marion Provost,^a Stefania Cacovich,^{a,b} Guillaume Vidon,^{a,b} Jean Rousset,^{a,d} Muriel Bouttemy,^{a,d} Nathanaelle Schneider^{a,b}

^aInstitut Photovoltaïque d'Ile-de-France (IPVF), 18 boulevard Thomas Gobert, 91120 Palaiseau, France

^bCNRS, UMR-IPVF 9006, 18 boulevard Thomas Gobert, 91120, Palaiseau, France

^cInstitut Lavoisier de Versailles (ILV), Université de Versailles Saint-Quentin en Yvelines, Université Paris-Saclay, CNRS, UMR 8180, 78035 Versailles Cedex, France

^dEDF R&D, 18 boulevard Thomas Gobert, 91120 Palaiseau, France

Type of communication: Poster

Atomic Layer Deposition (ALD) is increasingly contributing to the energy field and more specifically to the engineering of solar cells. Its conformity enables deposition on nanostructured substrates and its low growth temperature allows the deposition on temperature-sensitive substrates such as perovskite [1,2,3]. Niobium oxide, Nb₂O₅, is a wide bandgap semiconductor that has been grown by different methods and has recently been used in solar cells. Its optical and electrical properties depend strongly of the technique used for its growth, opening access to a wide range of application, such as electron transport layer (ETL) or passivation layer [4,5]. It is also used for the doping of titanium oxide (TiO₂), a well-known ETL, to reach a better stability of the complete solar cell.

In this study, the growth of niobium-doped titanium oxide (TiO₂:Nb) thin films by atomic layer deposition (ALD) and its use to extract photogenerated electrons is reported. Films were obtained at 200°C from titanium (IV) i-propoxide (TTIP), (t-butylimido)tris(diethylamido)niobium(V) (TBTDEN), and water by introducing Nb₂O₅ growth cycle in a TiO₂ matrix. Process parameters such as the order of precursor introduction and the cycle ratio were optimized. The growth mechanisms and the effective Nb incorporation were investigated by in situ quartz crystal microbalance (QCM) and X-ray photoelectron spectroscopy (XPS). The as-deposited films were analyzed for their surface morphology, elemental stoichiometry, optoelectronic properties, and crystallinity using a variety of characterization techniques. Such as-deposited films are amorphous and a fine control of the Nb amount with the supercycle parameters along with a continuous evolution of their optical properties from the ones of TiO₂ to Nb₂O₅ bare oxides are observed. To allow a successful implementation in solar devices, a comprehensive annealing study under several temperatures and atmospheres was conducted and revealed an evolution of the optical bandgap after crystallization in the anatase phase. Ultimately, the incorporation of these 15 nm-thick films in mesoscopic perovskite solar cells (PSCs) as ETL shows an improvement of the cell performances and of their stability with increasing Nb amount, in comparison of both TiO₂ and Nb₂O₅ pure compounds, reaching power conversion efficiency (PCE) up to 18.3% and a stability above 80% of its nominal value for 138 h under illumination.

[1] Park, (2021). *Nanomaterials*, 11, 88. <https://doi.org/10.3390/nano11010088>

[2] Xing, et al, (2020), *Small Methods*, 4, 2000588. <https://doi.org/10.1002/smt.202000588>

[3] Raiford, et al, (2020) *Energy & Environmental Science*, 13, 1997–2023. <https://doi.org/10.1039/D0EE00385A>

[4] Subbiah, et al, (2019). *Energy Technology*, 8(4), 1900878. <https://doi.org/10.1002/ente.201900878>

[5] Macco, et al, (2018). *Solar Energy Materials and Solar Cells*, 184, 98-104. <https://doi.org/j.solmat.2018.04.037>



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Photoluminescence and Ellipsometry spectroscopies embedded in a ALD platform to control and analyze perovskites thin film and interfaces

Nao HARADA^a, Alexandra LEVTCHENKO^a, Damien COUTANCIER^b,
Frederique DONSANTI^a, Julie GOFFARD^a, Corentin DOMENEGHETTY^a,
Jean-François GUILLEMOLES^b, Daniel SUCHET^b, Géraud DELPORT^b,
Nathanaelle SCHNEIDER^{b,*}

^a IPVF, Institut Photovoltaïque d'Île de France, 18 Boulevard Thomas Gobert, 91120 Palaiseau, France

^b IPVF, UMR 9006, CNRS, IPVF SAS, Ecole Polytechnique, PSL U., 18 Bld Th. Gobert, 91120 Palaiseau, France

* Corresponding author e-mail: geraud.delport@cnrs.fr

Type of communication: Poster

This poster is complement to the oral presentation of Nathanaelle Schneider, that presented the possibilities of Atomic layer deposition (ALD) for depositing thin films for solar cells applications. As the deposition is sequential and self-limiting, it is possible to control the thickness of the films and achieve high conformality and limited roughness. In addition, the deposition can be done at low temperatures (below 100°C) and allows the growth of a wide range of materials on different substrates. In the field of photovoltaics, ALD films are employed on an industrial scale (e.g. in PERC solar cells), but they are also used to deposit passivation or charge transport layers (ETL & HTL) for perovskite solar cells ... [1].

In this poster we will present our novel approach to implement in situ ellipsometry and photoluminescence (PL) spectroscopies that we are developing at IPVF. On one hand, spectroscopic ellipsometry (SE) allows us to obtain valuable information on the thickness and optical constants of the film are studied during growth [2]. On the other hand, PL spectroscopy [3,4] allows us to obtain valuable information on the energy levels or characteristic dynamics of the electrons involved in the photovoltaic processes (Fig. 1).

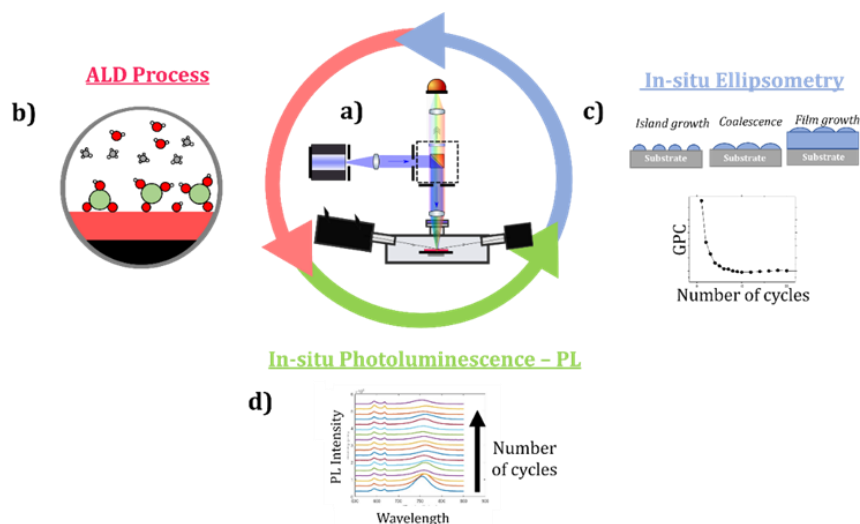


Figure 1. a) Experimental set-up with in-situ PL and ellipsometry in an ALD reactor b) ALD growth c) In situ ellipsometry - Thickness, optical constants, and growth mechanisms d) In situ PL – Functionalization properties (passivation, carrier behaviour)



JPH 2023

Journées Perovskites Halogénées

📅 31/05 – 02/06 📍 Biarritz, France

References

1. "Atomic Layer Deposition (ALD). Principes Généraux, matériaux et applications" *Ouvrage spécial des Techniques de l'Ingénieur : Principes et applications de la technique ALD (Atomic Layer Deposition)*
2. Langereis, E. et al. *J. Phys. Appl. Phys.* **42**, 073001 (2009).
3. Unold, T. & Gütay, L. in *Advanced Characterization Techniques for Thin Film Solar Cells* -275–297.
4. Kuhs, J. et al. *ACS Appl. Mater. Interfaces* **11**, 26277–26287 (2019).



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Copper-doped nickel oxide for inverted perovskite solar cells: Impact of Cu-doping and annealing temperature on PV cell parameters

Béchir DRIDI REZGUI¹, Firoz KHAN² and Jae Hyun KIM³

¹*Laboratoire de Photovoltaïque, Centre de Recherches et des Technologies de l'Énergie, Technopôle de Borj Cédria, BP 95, Hammam Lif, 2050 Tunis, Tunisie*

²*Interdisciplinary Research Center for Renewable Energy and Power Systems (IRC-REPS), Research Institute, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran 31261, Saudi Arabia*

³*Energy Convergence Research Group, Daegu Gyeongbuk Institute of Science & Technology (DGIST), 333 Techno Jungang-Daero, Hyeonpung-Myeon, Dalseong-Gun, Daegu-42988, South Korea*

Type of communication: Oral

The performance of an organic-inorganic perovskite solar cell (PSC) can be enriched via sinking the losses arisen in it. These losses are signified by the photovoltaic (PV) cell parameters (photogenerated current density (J_{ph}), shunt resistance (R_{sh}), series resistance (R_s), diode ideality factor (n), and reverse saturation current density (J_0)). Here, solution processed Cu-doped NiO_x (NiO:Cu) films were used as a hole transporting layer in inverted planar perovskite solar cells and the optoelectronic properties of NiO:Cu films as well as the PV performance of the resulting PSCs were systematically studied. The electrical properties of the PSCs were tuned by varying the Cu doping (0%, 5% and 10 %) and the annealing temperature (300, 350 and 400 °C). In particular, the study of the PV cell parameters of NiO:Cu-based PSCs revealed that the maximum value of J_{ph} was obtained for $R_{Cu/Ni} = 5\%$ and $t_{an} = 400$ °C. It is found that the R_{sh} value was enhanced by increasing $R_{Cu/Ni}$ and t_{an} , while the R_s was decreased with the increase of the annealing temperature with the minimal value attained at $R_{Cu/Ni}$ and t_{an} of 5% and 400 °C, respectively. Both n and J_0 increased with the rise in $R_{Cu/Ni}$ and t_{an} . Moreover, electrical measurements showed that PSC fabricated using 5% NiO:Cu-HTL annealed at 400 °C exhibits the highest PV performance with a short-circuit current density (J_{sc}) of 21.24 mA/cm², an open-circuit voltage (V_{oc}) of 1.031 V, a fill factor (FF) of 72.50 % and a power conversion efficiency (η) of 15.88%. The corresponding values of J_{ph} , R_{sh} , R_s , n and J_0 are 21.31 mA/cm², 1042.69 Ω.cm², 3.265 Ω.cm², 1.9739 and 3.025 x10⁻¹¹ A/cm², respectively. These encouraging results provide the possibility to further optimize the optical and electrical properties of NiO:Cu-HTLs and pave the way for the development of more stable and highly-efficient PSCs.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Synthesis of bismuth halide perovskite nanocrystals for photoelectrocatalytic CO₂ reduction

[A.Ghosh](#), V. Artero, and D. Aldakov

Univ. Grenoble Alpes, CEA, CNRS, INP, CEA IRIG, SyMMES, F-38000 Grenoble, France

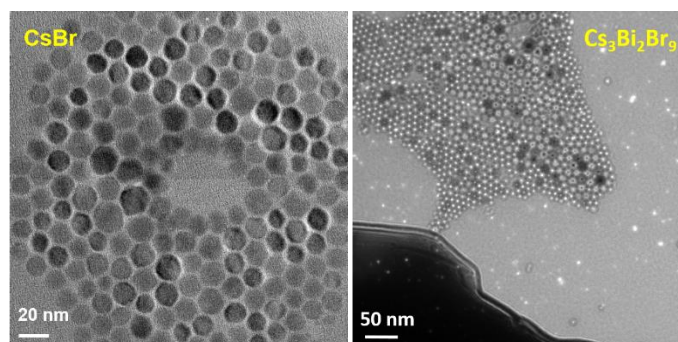
Univ. Grenoble Alpes, CNRS, CEA IRIG, LCBM, F-38000 Grenoble, France

antik.ghosh@cea.fr

Type of communication: Poster

Solar-driven CO₂ valorization into hydrocarbon fuels using semiconductor catalysts offers a promising energy conversion pathway to have impactful solutions to environmental degradation and energy crisis problems¹. The solar light not being sufficient to break the high energy C=O bond in CO₂, an external photosensitizer (PS) coupled to co-catalyst is used in this process. The PSs used presently are often hard to synthesize, they are toxic and have limited stability and light absorption capacity. Colloidal semiconductor nanocrystals (NCs) can have strong light absorption and stability; in addition, their properties can be easily optimized by the size and/or composition control. We propose to use halide perovskite NCs as PSs for the photoelectrocatalysis. The halogenated perovskites have been recently very successfully used for the photovoltaics; however, most of them are based on lead, a highly toxic element. In this work we propose to synthesize alternative perovskites based on bismuth, A₃Bi₂X₉ (A=cation; X=Br, I). These much less toxic NCs can have optoelectronic properties well adapted for the CO₂ photoreduction.

We have developed a new transformational approach to synthesize air-stable bismuth halide perovskites NCs in ambient conditions with a high reaction rate using cesium halide NCs as templates². By optimizing synthesis protocols, we managed to obtain air-stable Cs₃Bi₂Br₉ and Cs₃Bi₂I₉ NCs with the sizes of around 10 nm. Synthesis details, structural and optoelectronic properties will be discussed, as well as their perspectives for the photoelectrocatalysis CO₂ reduction applications.



References

[1] Zhang, K. et al. Current dilemma in photocatalytic CO₂ reduction: real solar fuel production or false positive outcomings? *Carbon Neutrality* 1, 1–16 (2022)

[2] Shamsi, J. et al. Colloidal CsX (X = Cl, Br, I) Nanocrystals and Their Transformation to CsPbX₃ Nanocrystals by Cation Exchange. *Chem. Mater.* 30, 79–83 (2018)



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

A theoretical framework to examine and tailor electronic and optoelectronic properties of halide double perovskites

[Mayank Gupta](#) and B. R. K. Nanda

Condensed Matter Theory and Computational Lab, Department of Physics, Indian Institute of Technology Madras, Chennai, India

Type of communication: Poster

Abstract: We present a comprehensive electronic and optical properties analysis using a semi-empirical tight-binding (TB) model for all possible inorganic halide double perovskites (HDP) of the general formula $Cs_2BB'X_6$. The orbital overlapping and the cause of large bandgap variations in pristine HDPs are successfully explained through the interactive molecular orbital pictures. With the help of TB Hamiltonian, we extended our model to supercell and obtained the interaction parameters for mixed cation HDPs ($Cs_2BB'_xB''_{1-x}X_6$ and $Cs_2B_xB'_{1-x}B''X_6$). We found that the hopping interactions are confined to the 2nd neighbour metal-to-metal; hence, the change in effective onsite energies can produce the electronic structures of HDPs for any value of x . Taking $Cs_2AgInCl_6$ as an example, we have studied the cation doping effect by replacing the Na atom at the Ag-site and the Bi atom at the In-site and explained the non-linearity of the bandgap as a function of cation concentration for each case. Our study shows that doping an additional transition metal cation at the B or B' site can produce octahedral distortion, which significantly changes the compound's band gap, parity, and position of VBM and CBM in the BZ. We have further extended the work to develop a model which is capable of analyzing the optical properties of pristine compounds and large supercells of mixed cation HDPs.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Introduction of phosphonic acid-based molecules as Self-Assembled Monolayers for MAPbI₃ perovskite solar cells

Y. Hami¹, F. Mameche¹, P. Decorse¹, P. Lang¹

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

Corresponding speaker: lang@u-paris.fr

Type of communication: Poster

To improve control of the electrode-halogenated perovskite interface in photovoltaic solar cells (PCS), we employ a strategy of grafting appropriately functionalized self-assembled monolayers (SAMs) either on the intermediate MO_x layers or directly on the ITO substrate.

Self-assembled hole transport monolayers (HTML) are introduced between the conducting electrodes (ITO) and the active layer with the primary purpose of enhancing device performance. The intended function of HTML is to adjust the electronic energy levels of ITO to match those of the halogenated perovskite (HP) layer, improving charge transfer and energy recovery, and optimizing the overall characteristics of the PCS.

The organic molecules used as HTML are synthesized and have the general structure H₂PO₃-(CH₂)₂-Cz-R₂ (Cz=carbazole, R in 3,6 positions = MeO, NH₂, -CH₂NH₂) (Figure 1). Their orientation has been determined to understand both their electronic effects as hole transport layers (HTLs) and their chemical interactions with the halogenated perovskite (HP) layer. We have then evaluated the photovoltaic performances of the complete PCS.

The grafting, orientation and structure of HTML have been investigated by IR spectroscopy (PM-IRRAS) and XPS. Their effects on the structure of the perovskite MAPbI₃ film have been analyzed by UV-Vis spectroscopy, X-Ray Diffraction and SEM.

In this study, we analyzed the influence of HTML (SAMs) on the photovoltaic performance and stability of perovskite solar cells. The effect was discussed with respect to the nature of terminal poles (NH₂, CH₂NH₂ vs. MeO) and the formation of a common plane with the perovskite layer. We discussed the work function of modified ITO, the growth of HP, and the orientation of the crystallization planes of the MAPbI₃ perovskite on HTML/ITO, particularly regarding the photovoltaic parameters of the PSC.

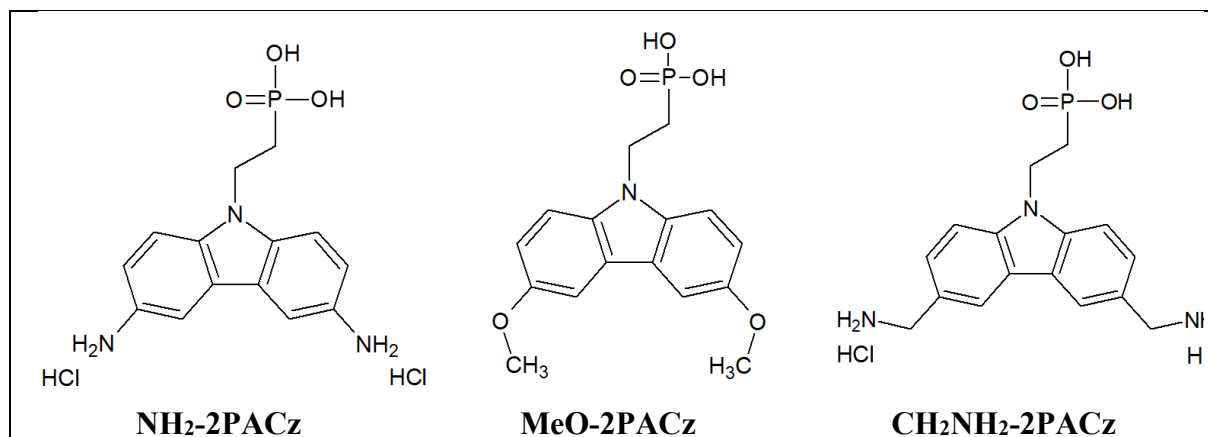


Figure 1. Chemical structure of the phosphonic molecule used.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Fabrication of All-Inorganic Perovskite CsPbBr₃ Thick Films using Close Space Sublimation

[J. Ihrenberger](#)¹, L. Grenet¹, F. Roux¹, F. Emieux¹, C. Anglade¹, E. Gros D'Aillon²

¹ Grenoble Alpes University, CEA, LITEN, DTNM, F38000 Grenoble, France

² Grenoble Alpes University, CEA, LETI, DOPT, F38000 Grenoble, France

Type of communication: Poster

In recent material research metal halide perovskites are of high interest due to their superior properties for photovoltaic and optoelectronic applications [1]. Especially CsPbBr₃ with its high stability against air and moisture [2] seems to be an interesting candidate for various applications like photovoltaics [3], neutron [4] and X-ray [5] detection. There are numerous fabrication routes for CsPbBr₃ which yield different type of products. Single crystals can be grown with solution based methods [6] or the Bridgman procedure [7]. Polycrystalline thin films are fabricated using spin coating [8], thermal evaporation [9] and other techniques. Polycrystalline thick films (<10 μ m) on the other hand are rarely investigated and no superior growth method has been found yet.

Addressing this gap, we present the usage of a straight forward physical vapour deposition technique called close space sublimation (CSS). A CsPbBr₃ precursor powder is made by ball milling raw powders of CsBr and PbBr₂. The so achieved perovskite powder is pressed to a target which is placed into a vacuum chamber made out of quartz glass. Outside placed halogen lamps heating up the target and the 3 or 5 mm distant substrate. At temperatures around 420 °C [10] the material starts to sublime and deposits at the substrate which is held at a lower temperature. The resulting polycrystalline films are examined using X-ray fluorescence and X-ray diffraction analyses showing high quality single phase CsPbBr₃ thick films with thicknesses ranging from 10 to 500 μ m. The film thickness with corresponding deposition speed was mapped over a large range of target temperatures. In general, higher temperatures yield faster but less even deposition. For one particular set of temperatures an advanced setup was used to measure the real temperature at target and substrate surface. This revealed a true temperature gradient of 25 °C while the set value was 100 °C.

- [1] W. Zhang, G. E. Eperon, and H. J. Snaith, "Metal halide perovskites for energy applications," *Nat. Energy*, vol. 1, no. 6, 2016, doi: 10.1038/nenergy.2016.48.
- [2] D. S. Tsvetkov, M. O. Mazurin, V. V. Sereda, I. L. Ivanov, D. A. Malyshkin, and A. Y. Zuev, "Formation Thermodynamics, Stability, and Decomposition Pathways of CsPbX₃ (X = Cl, Br, I) Photovoltaic Materials," *J. Phys. Chem. C*, vol. 124, no. 7, pp. 4252–4260, 2020, doi: 10.1021/acs.jpcc.9b11494.
- [3] S. Ullah *et al.*, "All-inorganic CsPbBr₃ perovskite: A promising choice for photovoltaics," *Mater. Adv.*, vol. 2, no. 2, pp. 646–683, 2021, doi: 10.1039/d0ma00866d.
- [4] L. Fernandez-Izquierdo, M. G. Reyes-Banda, J. A. Caraveo-Frescas, and M. Quevedo-Lopez,



JPH 2023

Journées Perovskites Halogénées

📅 31/05 – 02/06 📍 Biarritz, France

- “Inorganic Halide Perovskite Thin Films for Neutron Detection,” *Adv. Mater. Radiat. Detect.*, pp. 81–95, 2022, doi: 10.1007/978-3-030-76461-6_4.
- [5] Z. Gou *et al.*, “Self-Powered X-Ray Detector Based on All-Inorganic Perovskite Thick Film with High Sensitivity Under Low Dose Rate,” *Phys. status solidi – Rapid Res. Lett.*, vol. 13, no. 8, p. 1900094, Aug. 2019, doi: 10.1002/PSSR.201900094.
- [6] P. Sujith, M. Pratheek, S. R. Parne, and P. Predeep, “Growth and Characterization of High-Quality Orthorhombic Phase CsPbBr₃ Perovskite Single Crystals for Optoelectronic Applications,” *J. Electron. Mater.*, vol. 52, no. 1, pp. 718–729, 2023, doi: 10.1007/s11664-022-10042-w.
- [7] C. C. Stoumpos *et al.*, “Crystal growth of the perovskite semiconductor CsPbBr₃: A new material for high-energy radiation detection,” *Cryst. Growth Des.*, vol. 13, no. 7, pp. 2722–2727, 2013, doi: 10.1021/cg400645t.
- [8] L. Clinckemalie, D. Valli, M. B. J. Roeffaers, J. Hofkens, B. Pradhan, and E. Debroye, “Challenges and Opportunities for CsPbBr₃ Perovskites in Low- and High-Energy Radiation Detection,” *ACS Energy Lett.*, vol. 6, no. 4, pp. 1290–1314, 2021, doi: 10.1021/acsenenergylett.1c00007.
- [9] J. Li *et al.*, “Fabrication of efficient CsPbBr₃ perovskite solar cells by single-source thermal evaporation,” *J. Alloys Compd.*, vol. 818, 2020, doi: 10.1016/j.jallcom.2019.152903.
- [10] C. Zhang *et al.*, “Thermal stability of CsPbBr₃ perovskite as revealed by in situ transmission electron microscopy,” *APL Mater.*, vol. 7, no. 7, p. 071110, Jul. 2019, doi: 10.1063/1.5108849.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Amino-terminated SAMS for the functionalization of mp-TiO₂ in Hybrid Perovskite Solar Cells

A.Torkhani^{1,2}, F. Mameche¹, P. Decorse¹, Y.Hami, S. Derouich¹, F.Kouki², P. Lang¹

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

2: LMAPQ university El Manar; Tunis

Corresponding speaker: lang@u-paris.fr

The mastery of interfaces in Hybrid Perovskite (HP) Solar Cells remains an important challenge. Thanks to the functionalization of HTL and ETL based on MO_x by amino terminated Self-assembled Monolayers (SAMs, Fig.1), we aim to improve on the one hand, the growth of PH films and on the other hand the properties of the MO_x / PH interface via the MO_x work function or the reduction non-radiative recombination's [1]. We discuss here the structure-properties relationship of SAMs grafted on TiO₂-TiO₂mp and the structure and Photovoltaic performance of MAPbI₃ and triple cation FA_{0.83} MA_{0.17} Cs_{0.05} Pb (I_{0.83} Br_{0.17})₃ perovskite .

We demonstrate that the surface concentration of NH₃⁺ or (NH₃⁺+NH₂) groups conditions the morphology of MAPI and TC films as well as ultimately their PV properties. SAMs A and B, thanks to their flexibility brought by the CH₂ group, appear effective on both MAPI and TC films, while rigid SAMs S and C are only interesting for MAPI but little for TC which contains mostly formamidium.

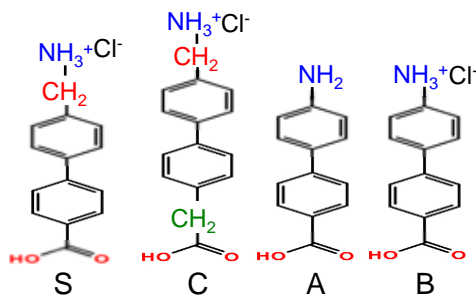


Figure 1: Chemical structures of molecules S, C, A and B of the SAMs

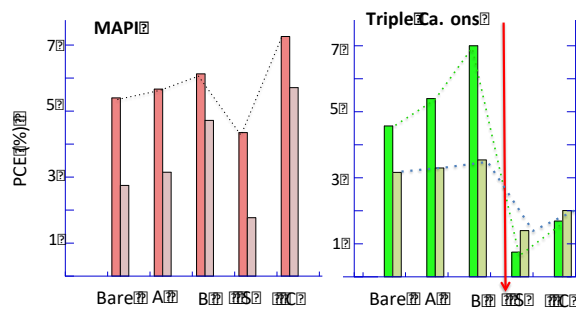


Figure 2: PCE versus the nature of the SAMs with the MAPI and the triple cations perovskite

References

[1] Tailor-Made Amino-Based Self-Assembled Monolayers Grafted on Electron Transport ZnO Layers: Perovskite Solar Cell Performance and Modified Interface Relationship H. Kouki, S. Pitié, A.Torkhani, F. Mameche, P. Decorse, M.Seydou, F. Kouki,* and P. Lang* ACS Appl. Energy Mater. 2022, 5, 1635–1645



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

On the necessity of similarity between the terminal function of an amino SAMs with the cation of the hybrid perovskite in a PV cell: advantage of a monooriented ZnO layer

A.Torkhani^{1,2}, S. Nowack¹, S. Pitié¹, M. Seydou¹, F. Kouki² P. Lang¹
1: ITODYS University of Paris Diderot, CNRS, 75205 Paris FRANCE
2: LMAPQ university El Manar; Tunis
Corresponding speaker: lang@u-paris.fr

Amino-SAMs grafted by a COOH function on the MOx intermediate layers condition the growth and the structure of the hybrid Perovskite (HP) such as MAPbI₃ (MAPI) and triple cation (TC) FA_{0.83} MA_{0.17} Cs_{0.05} Pb (I_{0.83} Br_{0.17})₃ perovskite; this effect can make large improvements in PV properties. The terminal pole -NH₃⁺ / NH₂ (ammonium/amine) and its surface concentration play an essential role in this structuring [1]. Here we address the cross-comparison of a -NH₃⁺/NH₂ pole and H₂N-CH⁺-NH₂ (amidinium) on the the properties of MAPI and of a PH TC. In order to fully understand the influence of the organization of these SAMs themselves, we used ZnO-based ETL either in the form of nanoparticles (NP), or in the form of a (002) monooriented (MO) layer of hexagonal ZnO synthesized by means of precursors.

The 3 steps of the cell building are analyzed : SAMs by PM-IRRAS, HP films by RX UV and solar cells. Concerning the effect of SAMs S, C (terminated by amine or ammonium) and PI (terminated by amidinium) (figure 1), we noted that those terminated at the same pole as the cation methylammonium or mostly formamidium, present in the PH give the best orientation of the films and the best PV performance and those whatever the ZnO substrate : S and C work best with MAPI and PI with TC. Finally, the use of ZnO MO removes all traces of PbI₂ in the two PH films compared to ZnO NP. Furthermore, the MO substrate leads to a PCE at least equal to those of ZnO NP, with even more than a doubling of the PCE of MAPI and TC for the bare substrate and the PI.

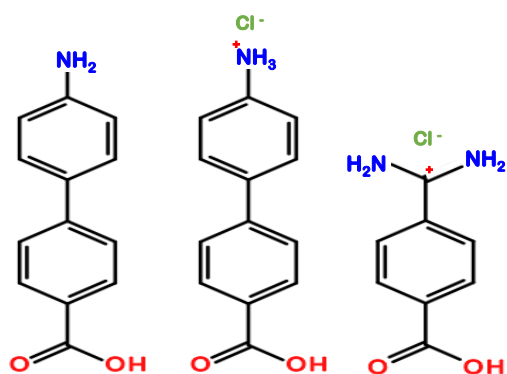


Figure 1: Chemical structures of molecules S, C, PI of the SAMs

References

[1] Tailor-Made Amino-Based Self-Assembled Monolayers Grafted on Electron Transport ZnO Layers: Perovskite Solar Cell Performance and Modified Interface Relationship
H. Kouki, S. Pitié, A.Torkhani, F. Mameche, P. Decorse, M.Seydou, F. Kouki,* and P.Lang*
ACS Appl. Energy Mater. 2022, 5, 1635–1645



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Solution Grown Thick Polycrystalline Halide Perovskite Monoliths for X-ray Detection

Thibault Lemerrier^a, Ferdinand Lédée^b, Stéphanie Lombard^c, Javier Mayén Guillén^c, Jean-Marie Verilhac^c, Eric Gros Daillon^b, Alain Ibanez^a, Julien Zaccaro^a

^a Grenoble Alpes University, CNRS, Grenoble INP, Institut Néel, F38042 Grenoble, France

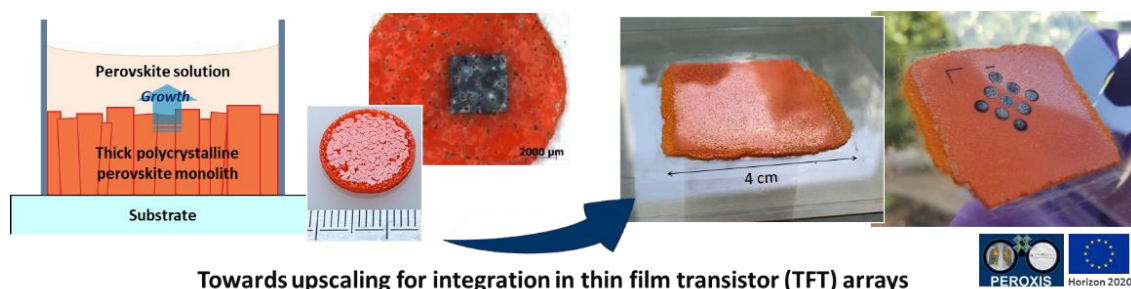
^b Grenoble Alpes University, CEA, LETI, DOPT, F38000 Grenoble, France

^c Grenoble Alpes University, CEA, LITEN, DTNM, F38000 Grenoble, France

Type of communication: Poster

Halide perovskites have very attractive optoelectrical properties for applications such as UV-visible photodetection and direct X-ray detection. The latter requires specifically much thicker perovskite layers to absorb most of the incoming X-rays so that the desired thickness is from one to several millimeters. Reaching such thicknesses by crystallization from solution cannot be done solely by nucleation of grains but puts an emphasis on their growth at the later stages of the fabrication process. As X-ray detectors in thin film transistor (TFT) arrays can be very large (*i.e.*, 40 x 40 cm²) to form an image in medical imaging for instance, the typical small grown single crystals are not sufficient to reach such a goal. On the opposite, polycrystalline layers are more suitable to make large surface coatings, but having them thick enough as well is still challenging and in progress [1, 2].

In this work, we propose a route to manufacture polycrystalline MAPbBr₃ perovskite monoliths that are millimeter-sized thick and from 1.5 to several centimeter-sized wide. We will present required conditions before (specific primer layer) and during growth that allow to obtain monoliths with a high crystalline orientation, that is to say preferentially columnar grown grains. Moreover, as the growth in solution of such thick samples unavoidably leads to free-standing monoliths (lifted-off from the substrate), an adhesion issue emerges in order to integrate a monolith onto a TFT array. Therefore, we will also discuss here about a solution that uses a UV-resin grid on the substrate, which helps its adhesion with the thick perovskite layer and allows to have some images under X-rays.



Towards upscaling for integration in thin film transistor (TFT) arrays

Figure 1. Schematic illustration of solution growth principle with examples of typical thick polycrystalline perovskite monoliths obtained in small and large size used for X-ray detection tests.

References

- [1] R. Tan *et al.*, « Characterization of solution grown 3D polycrystalline methylammonium lead tribromide for x-ray detection », *J. Appl. Phys.*, 132, 204503, 2020, doi: 10.1063/5.0100362.
- [2] Y. Haruta *et al.*, « Scalable Fabrication of Metal Halide Perovskites for Direct X-ray Flat-Panel Detectors: A Perspective », *Chem. Mater.*, 34, 5323-5333, 2022, doi.org/10.1021/acs.chemmater.2c00764.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Multi-resonances for simultaneous enhancement of two-photon absorption and photoluminescence extraction in perovskite metasurface

Tam Trong Nguyen¹, Raphael Mermet Lyaudoz¹, Quang-Huy Do², Johann Bouclé², Bernard Ratier², Rémi Antony Céline Chevalier¹, Emmanuelle Deleporte³, Emmanuel Drouard¹, Christian Seassal^{1,2}, Hai Son Nguyen^{1,2}

1. Univ Lyon, Ecole Centrale de Lyon, INSA Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, INL, UMR5270, Ecully 69130, France

2. XLIM UMR CNRS 7252, Université de Limoges, Limoges, France

3. Lumière, Matière et Interfaces (LuMI) Laboratory, Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupélec, 91190 Gif-sur-Yvette, France

Type of communication: Oral

Over the past decade, perovskites have gained significant attention as a highly promising candidate for the next generation of optoelectronic devices. Recent studies have demonstrated that the two-photon absorption in perovskite can be greatly enhanced by implementing photonic resonances at virtual absorption levels situated well below the perovskite bandgap [1,2]. Additionally, photoluminescence (PL) emission can be improved by harnessing photonic resonances at the emission wavelength [3]. In this work, we present an original photonic design for a perovskite metasurface that exhibits a double photonic effect: i) slow-light resonances at 750nm and 800nm for improving two-photon absorption, and ii) fast modes in the range of 540-580 nm for boosting emission extraction. As a proof-of-concept, we fabricated the quasi-2D perovskite metasurface using a thermal nanoimprint technique (Fig. 1a). We observed Bloch resonances for two-photon absorption in angle-resolved reflectivity measurements (Fig. 1b), and those for PL extraction in angle-resolved PL (Fig. 1c). Our work paves the way for engineering multi-resonant perovskite metasurfaces for use in future devices such as LEDs, detectors, lasers, and solar cells.

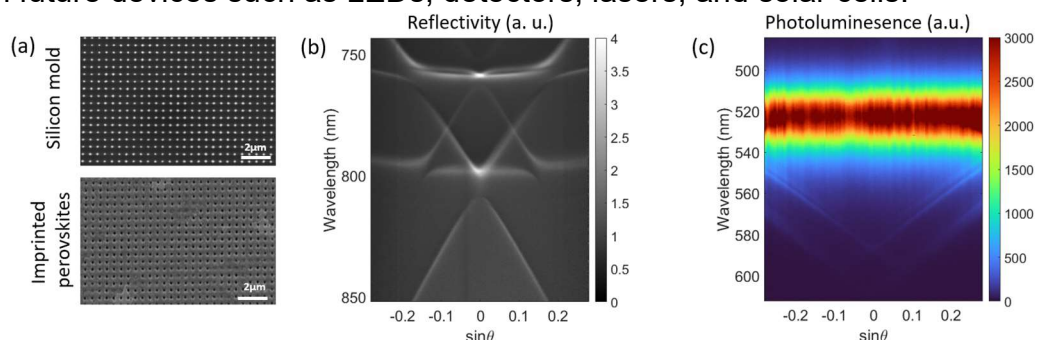


Figure 1. (a) SEM images of the mold and imprinted perovskite. (d,e) Angle-resolved reflectivity (d) and (e) PL spectra.

References

[1] C. Becker et al. ACS Photonics 5, 4668–4676 (2018).

[2] Y. Fan et al. Nano Lett. 21, 7191–7197 (2021)

[3] L. A. Muscarella et al. ACS Appl. Mater. Interfaces 14, 38067–38076 (2022).



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

First integration of amorphous carbon nitride layers in electrodeposited perovskite solar cells

Youssef Dandal^a, Rokaya El Otmani^b, Florence Billon^a, Cyrille Bazin^a, Françoise Pillier^a,
Ahmed El Manouni^b, Sidi Ould Saad Hamady^c, [Alain Pailleret^a](#)

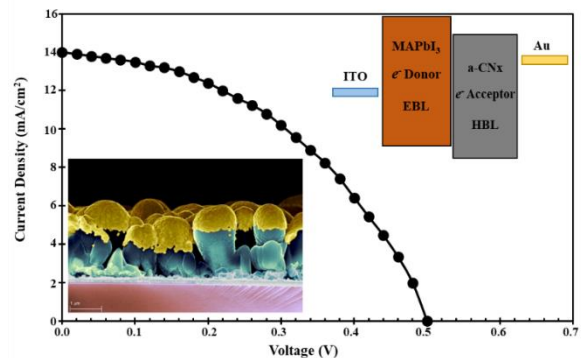
^aSorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques (LISE, UMR 8235), 4 place Jussieu, (case courrier 133), F-75005, Paris, France

^bLaboratoire LNMAMT, Département de Physique, Faculté des Sciences et Techniques, Université Hassan II, BP 145, Mohammedia, Morocco.

^cUniversité de Lorraine, CentraleSupélec, Laboratoire Matériaux Optiques, Photonique et Systèmes, EA 4423, Metz, F-57070, France

Type of communication: Oral

In this contribution, amorphous carbon nitride (a-CNx) thin layers [1, 2] were integrated in Perovskite Solar Cells (PSCs) for the first time. In a preliminary study, the structural and opto-electronic properties of each of the involved layers was carried out, and the role of each layer in the resulting photovoltaic cell was investigated. The complete solar cells were then developed and their photovoltaic parameters, including power conversion efficiency (PCE), open circuit voltage (VOC), external quantum efficiency (EQE) and fill factor (FF), were measured under AM 1.5 solar illumination. The best experimental PCE value, 3.01%, was measured on ITO/CH₃NH₃PbI₃/a-CNx /Au solar cells. The experimental measurements were validated with modeling studies performed with the 1D-SCAPS software and using input parameters extracted from opto-electronic properties of the a-CNx and perovskite layers. A theoretical PCE value of 3.64% was found to be in very good agreement with the experimental value. Based on this result, CH₃NH₃PbI₃/a-CNx heterostructures are promising candidates for the next generation of perovskite solar cells and deserve much more study, optimization and understanding for boosting their performances.



References

- [1] J.C. Byers *et al.*, ACS Appl. Mater. Interfaces, 4, 2012, 4579–4587.
- [2] J.C. Byers *et al.*, Russ. J. of Electrochem., 56(10), 2020, 859–867.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Synthesis of inorganic halide perovskite targets for pulsed laser thin film deposition

E.Parrat¹, F.Dupont¹, L.Grenet², O.Poncelet², M.Roumanie² and F.Templier¹

¹ Univ. Grenoble Alpes, CEA, LETI, F-38000 Grenoble, France

² Univ. Grenoble Alpes, CEA, Liten, DTNM, F-38000 Grenoble, France

Type of communication: Poster

Halide perovskite materials are direct bandgap semi-conductors with interesting electro-optical properties for opto-electronic devices such as LEDs, lasers and photovoltaics. However, perovskite devices suffer from instability when they are exposed to different parameters, for example oxygen, humidity, light and high temperature. This sensitivity is often linked with the presence of organic compounds in the perovskite. Hence, a possibility to address this problematic is to use inorganic halide perovskites, which could be intrinsically more stable.

Diverse deposition technics can be used to deposit inorganic perovskite thin films. Among them, pulsed laser deposition (PLD) is an interesting option. Indeed, during the PLD process, the stoichiometry of the target is largely transferred to the thin film ¹. However, the elaboration of the perovskite target used in PLD has not been extensively discussed in the literature until very recently ².

Here we have explored diverse options to synthesize PLD targets with various compositions: CsPbBr₃, CsPbI₂Br and CsPbI₃. First, we have evaluated two approaches to synthesize perovskite powder: milling of the precursors or crystallization in a solution. Then, we pressed the powder using a thermopress or a spark plasma sintering device, enabling us to control temperature and pressure during the process. Finally, different thermal annealing have been studied in order to densify the PLD targets. Overall, we tended to form homogeneous and dense targets with flat surfaces for each composition.

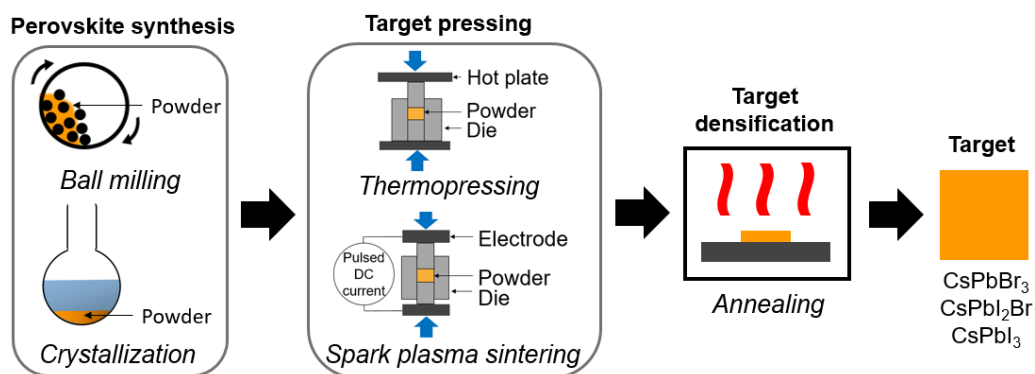


Figure 1. Elaboration path explored for inorganic perovskite PLD target synthesis.

References

1. Schou, J. Physical aspects of the pulsed laser deposition technique: The stoichiometric transfer of material from target to film. *Appl. Surf. Sci.* **255**, 5191–5198 (2009).
2. Zheng, L. *et al.* A universal all-solid synthesis for high throughput production of halide perovskite. *Nat. Commun.* **13**, 7399 (2022).



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Using Hansen solubility parameters to understand solvent-antisolvent interactions in metal halide perovskites

Oscar Telschow, Niels Scheffczyk, Alexander Hinderhofer, Lena Merten, Ekaterina Kneschaurek, Florian Bertram, Qi Zhou, Markus Löffler, Frank Schreiber, Jose Roberto Bautista-Quijano, Yana Vaynzof and [Fabian Paulus](#)

Type of communication: Poster

The solvent-engineering method is one of the most commonly employed deposition techniques for metal halide perovskites processed from solution. In this method, an antisolvent is applied towards the end of the spin-coating of the perovskite precursor solution, in order to trigger supersaturation and initiate the nucleation and solidification of the film.^{1,2} Despite extensive research, the solvent-antisolvent and precursor-antisolvent interactions and their implications on the deposition process and the film formation remain not completely understood. Here, we show that the degree of orientation of triple cation perovskite films is impacted by the choice of antisolvent. Specifically, the use of alcoholic antisolvents leads to highly oriented perovskite films, while other antisolvents lead to a random orientation. We demonstrate by in-situ grazing-incidence wide-angle X-ray scattering (GIWAXS) that alcoholic antisolvents result in a short-lived, highly orientated crystalline intermediate, which templates the resulting perovskite film. This templating becomes possible by the selective interaction of the alcoholic antisolvents with N,N-dimethyl formamide (DMF) in the host solvent mixture. The resulting photovoltaic devices fabricated from such highly oriented films are superior to those with a random polycrystalline microstructure in terms of both performance and stability.³ We suggest that solvent-antisolvent and precursor-antisolvent interactions can be rationalized by considering the Hansen Solubility Parameters (HSP).⁴ The evaluation of the distances in HSP-space between the various solvents and antisolvents makes it possible to propose generalized guidelines for the selection of the optimal solvent-antisolvent systems.

References

- [1] M. Xiao, F. Huang, W. Huang, Y. Dkhissi, Y. Zhu, J. Etheridge, A. Gray-Weale, U. Bach, Y.-B. Cheng and L. Spiccia, *Angewandte Chemie International Edition*, 2014, 53, 9898–9903
- [2] Taylor, A.D., Sun, Q., Goetz, K.P. et al. A general approach to high-efficiency perovskite solar cells by any antisolvent. *Nat Commun*, 2021, 12, 1878
- [3] O. Telschow, N. Scheffczyk, A. Hinderhofer, L. Merten, E. Kneschaurek, F. Bertram, Q. Zhou, M. Löffler, F. Schreiber, F. Paulus, Y. Vaynzof *Elucidating Structure Formation in Highly Oriented Triple Cation Perovskite Films*, *Adv. Sci.*, 2023, 22006335
- [4] C. M. Hansen *The three dimensional solubility parameter and solvent diffusion coefficient: Their importance in surface coating formulation*. Doctoral Dissertation, 1967, Technical University of Denmark



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Band-Edge Exciton Fine Structure and charge-carrier interactions in Lead-Halide Perovskite Nanocrystals

E. Prin, P. Tamarat, B. Lounis

LP2N, Univ. Bordeaux, IOGS & CNRS, Talence (France)

Type of communication: Poster

Lead-halide perovskite nanocrystals (NCs) have emerged as attractive nano-building blocks for photovoltaics and optoelectronic devices. Optimization of perovskite NC-based devices relies on a better knowledge of the fundamental electronic and optical properties of the band-edge exciton, whose fine structure has long been debated. This poster will give an overview of our recent magneto-optical spectroscopic studies [1-3] revealing the entire excitonic fine structure and relaxation mechanisms in these materials, using a single-NC approach to get rid of the inhomogeneities in the NC morphologies and crystal structures. Moreover, it will highlight universal scaling laws relating the exciton fine structure splitting, the trion and biexciton binding energies to the band-edge exciton energy in lead-halide perovskite nanocrystals, regardless of their chemical composition (inorganic and hybrid organic-inorganic, as well as mixed halide alloys) and their spectral emission range (from the blue to the near infrared). These scaling laws offer a general predictive picture for the charge-carrier interactions in these emerging materials, from the bulk regime to the regime of highly confined carriers.

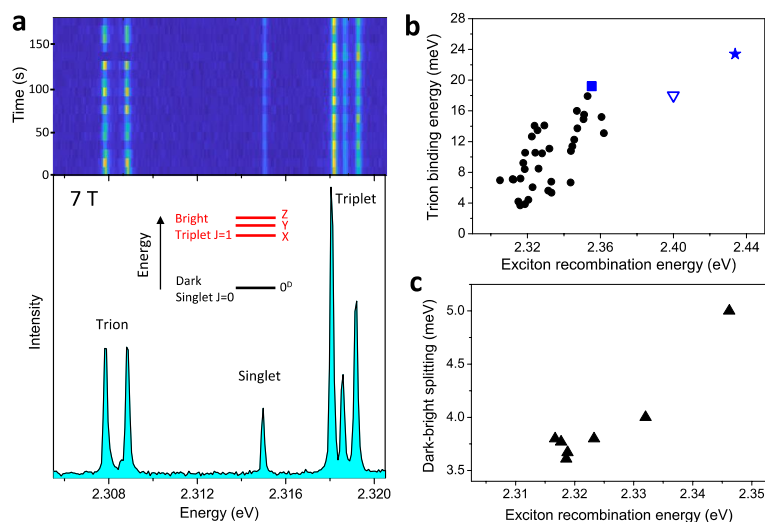


Figure 1. Band-edge exciton fine structure and trion binding energy in CsPbBr₃ NCs. [3]

References

- [1] Tamarat, P., Hou, L., Trebbia, J.-B., Swarnkar, A., Biadala, L., Louyer, et al., 2020. Nat Commun 11, 6001.
- [2] Hou, L., Tamarat, P., Lounis, B., 2021. Nanomaterials 11, 1058
- [3] Tamarat, P., Prin, E., Berezovska, Y., Moskalenko, A., Nguyen, T.P.T., Xia, C., et al., 2023. Nat Commun 14, 229.



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Modification of the light emission properties of individual inorganic perovskite nanocrystals using a versatile photonic structure

Z. Said, M.-R. Amara, A. Borel, C. Voisin, Y. Chassagneux, C. Diederichs*

Laboratoire de Physique de l'École Normale Supérieure, ENS, Université PSL, CNRS, Sorbonne Université, Université de Paris Cité, F-75005 Paris, France

* carole.diederichs@phys.ens.fr

Type of communication: Poster

Organic and inorganic lead halide perovskite nanocrystals (pNCs) have been intensively studied in the recent years for their outstanding optical properties such as the high brightness (quantum efficiencies up to 90%), the tunable optical bandgap, the reduced blinking, and the easy and low-cost fabrication. These features place them as good candidates to make a new generation of optoelectronics devices such as light emitting diodes (LEDs), lasers, photodetectors, or even liquid crystal displays (LCD). At the individual nanocrystal level, single photon emission at room temperature [1] and long coherence times at cryogenic temperature [2,3] have been observed. These characteristics are very promising to use pNCs as building blocks for efficient single photon generation for quantum optics and quantum communication applications.

In this context, the coupling of single pNCs to an optimized photonic structure is an important step to efficiently collect the emitted photons. Moreover, cavity Quantum Electro-Dynamics (cQED) effects could then be exploited to control and accelerate the nano-emitters spontaneous emission in the weak coupling regime (i.e., Purcell effect). In a longer-term perspective, more advanced cQED effects could also be used to realize photonic logic gates in the strong coupling regime.

Recently, we have designed and implemented a reconfigurable opened fiber-based microcavity which is especially suitable for CsPbBr₃ pNCs. It is based on a very versatile setup that was previously successfully optimized for single carbon nanotubes [4]. It is composed of a planar mirror and a concave mirror at the end of a fiber inserted in a movable lens, allowing us to study the same nano-emitter in free space and in cavity. In contrast to more conventional monolithic microcavities that must be designed for one specific emitter and cannot be modified afterward, the fibered microcavity is perfectly suited for solution-processed nano-emitters such as pNCs that are randomly dispersed on a substrate (the planar mirror here). After having precisely characterized our fibered-microcavity which has a Finesse of $\mathcal{F}=3000$ for an emission from 470nm to 550nm, we have observed the coupling of a single pNC with the cavity. With such promising results, a Purcell factor of several tens is expected with the entire size range of CsPbBr₃ pNCs. These first results open the way to the realization of a narrow and efficient single photon source at the cavity resonance frequency in the weak coupling regime.

References

- [1] [1] - Park et al., ACS Nano 9, 10386 (2015)
- [2] - Utzat et al., Science 363, 1068 (2019)
- [3] - Lv et al., Nano Lett. 19, 4442 (2019)
- [4] - Jeantet et al., PRL 116, 247402, (2016)



JPH 2023

Journées Perovskites Halogénées

31/05 – 02/06 Biarritz, France

Tin iodide perovskites with methylammonium activated by Self-Assembled Monolayers for solar cell efficiency and stability

B. Slimi^{1,2}, Y. Hami¹, F. Mameche¹, A. Torkhani¹, R. Chtourou², P. Lang¹

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

2: CRTE n, Research and Technology Center of Energy, Technopark Borj Cedria, Tunisia

Corresponding speaker: lang@u-paris.fr

Type of communication: Poster

Perovskite solar cells have attracted much attention as the potential next generation of photovoltaics. Especially, solar cells that use tin-lead halide perovskites as light-harvesting materials have been intensively studied.

There is, however, an environmental concern regarding toxic element lead inside of the perovskite structure, for which reason lead might be replaced with a nontoxic metallic element such as tin. For this reason, pure tin perovskite ($\text{CH}_3\text{NH}_3\text{SnI}_3$) solar cells have been developed. For the improve of the growth and stability of halogenated perovskite (HP) employed in photovoltaic solar cells, our aim is to employ the grafting strategy of appropriate functionalized Self-Assembled Monolayers (SAMs) onto the intermediate MO_x layers. Methylammonium tin iodide (MASnI_3) [1,2] is a lead-free hybrid perovskite (HP) with excellent optical versus electrical properties. This work introduces a process for growing high-purity and stable MASnI_3 thin films thanks to deposition of a suitable SAM on MO_x (Fig. 1). Afterwards, for the solar cells with halogenated perovskite, with the primary purpose of enhancing device performance. Electron transport layers (ETL) are inserted between the conducting electrodes (FTO, metals) and the active layer. The intended function of Self-Assembled Monolayers (SAMs) is to tune both chemical interaction and the electronic energy levels of the MO_x layers to match those of the halogenated perovskite (HP) layer, thereby optimizing the overall characteristics of the active film.

The molecule used in this work: Molecule B terminated with Amino group [$\text{HO}_2\text{C}-\text{CH}_2-\text{PP}-\text{CH}_2-\text{NH}_3\text{Cl}$ (B)] [3] and $\text{C}_8\text{H}_9\text{ClN}_2\text{O}_2$ (PI) grafted on MO_x layers such as mesoporous TiO_2 (mp- TiO_2) which has the role of (ETL). SAMs grafting have been analyzed by IR spectroscopy (ATR). Then we studied and compared the influence of such SAMs on the growth structure and stability of MASnI_3 perovskite film by UV-Vis spectroscopy, XR diffraction and Scanning Electron Microscopy SEM.

In this study, we highlight the influence of SAMs on photovoltaic performances and stability of perovskite solar cells. This effect is due to the terminal poles (NH_3^+ Cl⁻) which may constitute a common plane with the perovskite layer simultaneously allowing better growth with larger grains, orientation of the crystallization planes of the MASnI_3 and afterwards improving the photovoltaic performance of the solar cells.

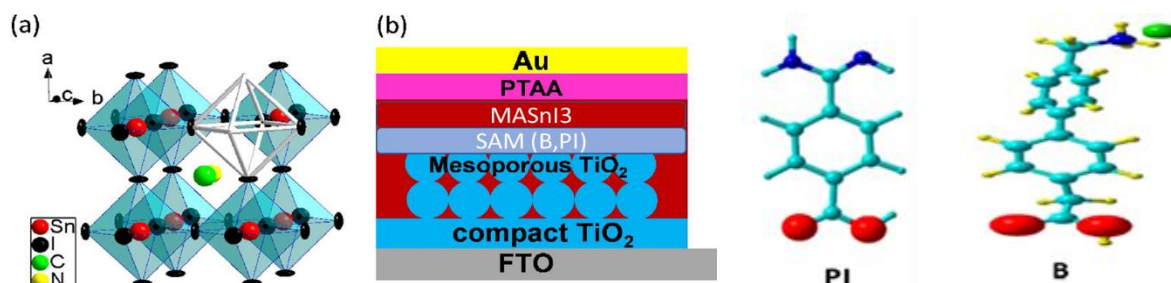


Figure 1. Schematic view of (a) Perovskite-based cells deposited on a mp- TiO_2 layer functionalized by self-assembled monolayers SAMs and (b) SAMs (B and PI)

References

- [1] C. Wang, Y. Zhang, F. Gu, Z. Zhao, H. Li, H. Jiang, Z. Bian, Z. Liu, *Matter* **2021**, 4, 709.
- [2] B. B. Yu, Z. Chen, Y. Zhu, Y. Wang, B. Han, G. Chen, X. Zhang, Z. Du, Z. He, *Adv. Mater.* **2021**, 33, 2102055.
- [3] H. Kouki, S. Pitié, A. Torkhani, F. Mamèche, P. Decorse, M. Seydou, F. Kouki, P. Lang *ACS Appl. Energy Mater.* 2022, January 27, 2022 <https://doi.org/10.1021/acsaem.1c03050>

