

Title: **Organic cation segregation and degradation in perovskite solar cells:a neutron scattering study**

1-04-170

Proposer (to whom correspondence will be addressed)

Name and first name	Address	Phone	Email
Jose Maria PORRO AZPIAZU	BCMATERIALS ,DERIO IBAIZABAL BIDEA EDIFICIO 500 PARQUE TECNOLÓGICO DE BIZKAIA 48160 DERIO SPAIN		jm.porro@bcmaterials.net
		New neutron user: No	New ILL user: No
Local contact contacted: Yes			

Co-proposers

Name and first name	Laboratory	Country
SAERBECK Thomas	ILL, GRENOBLE	INSTITUT LAUE-LANGEVIN
SALADO Manuel	BCMATERIALS ,DERIO	SPAIN

Local contact(s): **HONECKER Dirk, SAERBECK Thomas**

Suggested keyword number: **1-04**

This proposal is:

- A new proposal
 A continuation proposal
 A resubmission

Main research area: **Materials**

Submitted to other facilities: **No**

Societal indicators: **Earth & Environment/Energy**

Industry: **NOT related to industrial**

Unavailable dates:

Laboratory support facility

- Simulation support (C-lab) SAXS support through PSB Containment level 2 biology lab
 Chemistry Labs
 MSSL PSCM lab EMBL lab

Instruments

Requested instrument	Days
D17	6
D33	6

Requested starting time

1. Jan/Feb 2. Mar/Apr 3. May/June
 4. Jul/Aug 5. Sep/Oct 6. Nov/Dec

Comment: **The reflectometry measurements will be performed in D17 and the SANS ones in D33**

Sample availability: **Ready**

Instruments' logical connection: **D17 AND D33**

Experimental details

Energy/Wavelength range: **2-27Å**

Resolution in energy or wavelength: **2-10%**

Range of momentum transfer:

Resolution in momentum transfer:

To be filled in by ILL

Sample environment code	Comments by Health Physics Officer and Safety Engineer
AHC	

Abstract

In recent years, perovskite solar cells (PSC), have stunned the photovoltaic field owing to their unique combination of high performance and low-cost fabrication process. Compared with the existing technology, PSCs have demonstrated their potential by establishing an unprecedented increment in the power conversion efficiency (PCE) from 3.8% to >23.2% in less than a decade. Typically, hybrid perovskites are used, where the organic cations inside the perovskite satisfy the Goldschmidt tolerance factor, but present an orientational disorder in the crystal which increases with the temperature. In this context, in the present proposal we aim to perform a combination of neutron reflectometry and SANS experiments to study the structural part of the perovskite layer of the solar cells, paying special attention to the degradation of the perovskite and the organic cation segregation inside the perovskite structure. We will add up the results of these experiments with measurements of the PCE of each sample fresh and degraded. This will provide us with a scenario where we will be able to correlate the efficiency of the PSC with the degradation and organic cation distribution in the perovskite layer.

Sample description

Substance/Formula: Si/[(MA)_x(FA)_{1-x}]PbI₃	Substance/Formula: Si/[(MA)_x(Cs)_{1-x}]PbI₃
Mass (mg): Size (mm ³): 1600 Surface area (mm ²): 400 Space group: Container: Unit cell dimension: a = b = c = T(k)= α = β = γ = Solvent SLD: Particle SLD:	Mass (mg): Size (mm ³): 1600 Surface area (mm ²): 400 Space group: Container: Unit cell dimension: a = b = c = T(k)= α = β = γ = Solvent SLD: Particle SLD:
Substance/Formula: Si/MAPbI₃	Substance/Formula: Si/FAPbI₃
Mass (mg): Size (mm ³): 1600 Surface area (mm ²): 400 Space group: Container: Unit cell dimension: a = b = c = T(k)= α = β = γ = Solvent SLD: Particle SLD:	Mass (mg): Size (mm ³): 1600 Surface area (mm ²): 400 Space group: Container: Unit cell dimension: a = b = c = T(k)= α = β = γ = Solvent SLD: Particle SLD:

Sample environment equipment (supplied by ILL)

Environment equipment: **Humidity Chamber**

Laser: **None**

Use of gas: **None**

Temperature range:

Pressure range:

Magnetic field strength:

Danger associated with ancillary equipment: **Yes** **Uncertain** **No**

Safety aspects

The sample is: * **TOXIC**

Danger associated with the sample preparation: **Yes** **Uncertain** **No**

Danger associated with the sample handling: **Yes** **Uncertain** **No**

Type of waste to be processed after experiment: **Chemical** **Biological** **Nanoparticles** **Radioactive**

Publication

1. Background.

In recent years, perovskite solar cells (PSCs), have stunned the photovoltaic field owing to their unique combination of high performance and low-cost fabrication process.^[1,2] Compared with the existing technology, PSCs have demonstrated their potential by establishing an unprecedented increment in the power conversion efficiency (PCE) from 3.8%^[3] to >23.2% (<http://www.nrel.gov/ncpv/>) in less than a decade.

Typically, hybrid perovskites like $\text{CH}_3\text{NH}_3\text{PbI}_3$ are used. The methylammonium cation satisfies the Goldschmidt tolerance factor ($t=0.89$), but presents an orientational disorder in the crystal which increases with the temperature. In this circumstance, three different crystal phases occur at different temperatures. Larger organic cations such as formamidinium, which involves a tolerance factor close to one, have also been employed. However, formamidinium based perovskite exhibit a corner sharing α -phase perovskite structure or a face-sharing δ -phase perovskite when the film is annealed above or under 150°C , respectively.^[4]

In order to develop stable perovskite solar cells, different approaches were carried out. In previous works, Salado et al.^[5] studied the mixture of methylammonium (MA^+) and formamidinium (FA^+), and the results show that the addition of 20% MA avoided the undesirable formation of the δ -phase while maintaining the red-shifted band gap of FAPbI_3 , obtaining the best result with an addition of 40% MA. Recently, Yi et al.^[6] demonstrated that the best performance of the mixture was only with the addition of 10% MA. A stable “quasi-cubic” phase at room temperature is formed, achieving impressive efficiencies of 20.2%. Other inorganic cations were also used such as Cs or Rb^[7], paving a way towards replacement of organic cations in lead halide perovskites. In addition, triple cations (MA)/(FA)/(Cs) have been studied by different groups, showing that the addition of a low percentage of Cs, helping stabilizing the structure and increasing its thermal stability.^[8,9] Seok et al.^[10] demonstrated that a careful control of the growth conditions of perovskite layers, taking into account deficiency in halide anions, is essential for achieving high-efficiency devices. Although, with the addition of a mixture of different cations and halides devices a higher crystalline and stable perovskite is obtained, some reports indicate the existence of a non-perfectly homogeneous crystalline structure, but by a nanoscale segregation of multiple perovskite compositions.^[11]

2. Scientific case.

It is well known that the microstructure and phase purity of the films rely on the perovskite formation processes. A variety of different deposition techniques have been used with the aim to achieve high quality perovskite layer, such as two step (sequential) deposition^[12], vacuum evaporation^[13], vapour-assisted deposition^[14], or recently solvent engineering approach.^[15] However, even if the correlation between material quality and device performance has been extensively studied, a complete understanding of the degradation rate under external agents and cation segregation phases of perovskite remains unexplored. This is a major concern regarding the commercialization of this technology, where several factors, including temperature and humidity, among others, affect the long term stability of the devices under operating conditions^[16]. Despite considerable and successful research efforts to increase the PCE, relatively little progress has been made to understand the degradation mechanism of the PSCs, and to overcome the stability problems of these materials. Different strategies, such as crosslinking, doping, passivating, shielding with molecularly designed materials or enveloping the perovskite molecular structure in a foreign chemical environment, have been reported for improved humidity and UV-induced degradation (See Fig.1 bottom centre). However, increases in stability generally result in reduced PCEs.

In this context, within the present proposal we plan to perform a combination of neutron reflectometry and SANS experiments aiming at studying the structural part of the perovskite layer of the solar cells, paying special attention to the organic cation segregation inside the perovskite structure. The samples under study here will be composed of a 200nm thin film layer of perovskites of different compositions, spun-coated on top of a silicon block acting as a substrate. In order to avoid the effect of the roughness of the perovskite layer, after a discussion with the instrument scientist we decided to perform the reflectometry measurements with the incident beam coming from the substrate side, thus being sensitive to any changes in the perovskite layer at depths close to the interface with the substrate. In particular, we aim at obtaining information about two differentiated, but related, processes happening in the PSC samples: (i) the effect of degradation in both the organic cation(s) and the inorganic structure, and (ii) the segregation of the cations within similar crystal structures in different PSC samples. The degradation process of the PSCs happens as follows: $(\text{MA})\text{PbI}_3 \xrightarrow{T, \%} (\text{MA})\text{I} + \text{PbI}_2 + \text{HI}(g)$, where (MA) is the organic cation in this particular case.^[17] A combination of reflectometry and small angle measurements is proposed in order to get information about the effect of the degradation and cation segregation processes in the PSCs.

The reflectometry measurements will provide information about the depth profile of the PSCs once the degradation process is initiated, where thin layers of the resulting compounds (MA)I and PbI_2 will coexist with the initial (MA) PbI_3 PSC layer. Following previous studies, we suggest that the degradation process in these samples consists in the formation of a PbI_2 thin film at the bottom interface between the perovskite layer and the substrate.^[18,19] The time evolution of this process under temperature, humidity or UV light irradiation conditions will be studied with this technique for samples with four different cation compositions: only methylammonium, only formamidinium, a mixture of cations of methylammonium and formamidinium, and the last one with a mixture of an organic cation and an inorganic one (Caesium).

It is well known that in perovskites formed by mixed organic cations, organic cation segregation occurs.^[20–23] This results in the formation of a particular cation-rich regions inside the perovskite thin film. With a small angle neutron scattering experiment in PSCs of fresh samples with the aforementioned compositions, together with measurements of the samples after being degraded, we will be able to get information about:

- The amount of segregated cation in each PSC sample (for multiple cation compositions).
- The homogeneity degree of the cations within the perovskite layer of the PSC samples. This is expected to change between a fresh sample (where a homogeneous distribution is expected to occur) and a degraded one (where segregation of cations MA/FA/Pb²⁺ is expected to happen).
- If a structure factor appears, we would be able to estimate the mean distance among the segregated cations, which will be different in fresh and degraded samples.
- The effect of different degradation agents (temperature, humidity, UV light exposure) on the segregation effect of the cations site inside the perovskite structure, correlated with the depth profiles obtained with NR.

A previous study shows crystallite sizes of OSCs with MA cations in the range of 30 to 400nm^[24], a length scale resolvable with SANS. We will add up the results of these NR and SANS experiments with measurements of the PCE of each sample fresh and degraded. This will provide us with a scenario where we will be able to correlate the efficiency of the PSC with the degradation and organic cation distribution inside the perovskite structure of each sample.

Due to the low scattering cross section of the organic compounds with X-Rays it is not possible to perform any experiment involving this type of radiation with our PSC samples, thus making it possible only with small-angle neutron scattering measurements, where the scattering length density of organic materials is high enough. In order to distinguish between the different organic cations, present inside the same PSC, we will deuterated one of them in order to differentiate its SLD with respect to the other cation.

3. Experimental plan

For both the reflectometry and SANS experiments, we plan to measure the degradation processes of four different sample compositions at three different temperatures, and three relative humidity values, combined with exposure and non-exposure to UV light, making a total of 48 measurements. By performing scans of 2.5 hours for each experiment type, the total measurement time in each instrument will be 120 h. Adding up the necessary time to set up the measurements, we request a total of 6 days in each instrument for both the NR and SANS measurements.

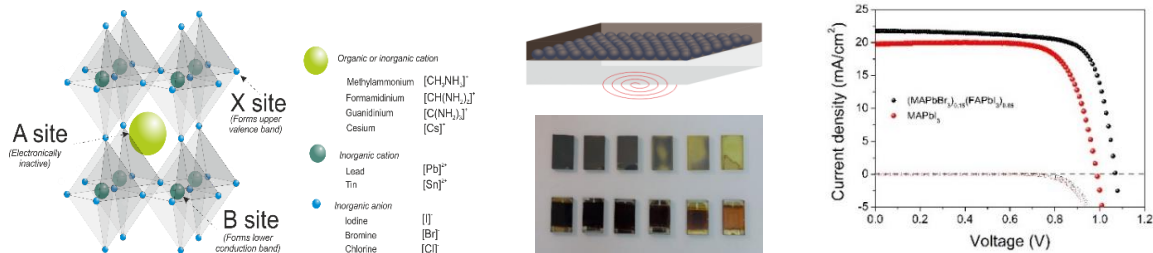


Figure. (Left) Perovskite structure and position of the different elements that can compose it. (Top center) Scheme of Perovskite sample with mesoscopic structure. (Bottom center) Perovskite film degradation process (left to right) after 90 days in humidity conditions. (Right) J-V curve of MAPbI₃ and mixed perovskite.

References

- [1] N. G. Park, *Mater. Today* **2015**, *18*, 65–72.
- [2] M. A. Green, A. Ho-Baillie, H. J. Snaith, *Nat. Photonics* **2014**, *8*, 506–514.
- [3] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050–6051.
- [4] A. Binek, F. C. Hanusch, P. Docampo, T. Bein, *J. Phys. Chem. Lett.* **2015**, *6*, 1249–1253.
- [5] M. Salado, L. Calio, R. Berger, S. Kazim, S. Ahmad, *Phys. Chem. Chem. Phys.* **2016**, DOI 10.1039/C6CP03851D.
- [6] Y. Zhang, G. Grancini, Y. Feng, A. M. Asiri, M. K. Nazeeruddin, *ACS Energy Lett.* **2017**, *2*, 802–806.
- [7] M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt, et al., *Science (80-.)* **2016**, *354*, 206–209.
- [8] M. Deepa, M. Salado, L. Calio, S. Kazim, S. M. Shivaprasad, S. Ahmad, *Phys. Chem. Chem. Phys.* **2017**, *19*, 4069–4077.
- [9] M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, et al., *Energy Environ. Sci.* **2016**, *9*, 1989–1997.
- [10] W. S. Yang, B. W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, S. S. Shin, J. Seo, E. K. Kim, J. H. Noh, et al., *Science (80-.)* **2017**, *356*, 1376–1379.
- [11] P. Gratia, G. Grancini, J. N. Audinot, X. Jeanbourquin, E. Mosconi, I. Zimmermann, D. Dowsett, Y. Lee, M. Grätzel, F. De Angelis, et al., *J. Am. Chem. Soc.* **2016**, *138*, 15821–15824.
- [12] J. Burschka, N. Pellet, S. J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel, *Nature* **2013**, *499*, 316–319.
- [13] M. Liu, M. B. Johnston, H. J. Snaith, *Nature* **2013**, *501*, 395–398.
- [14] Q. Chen, H. Zhou, Z. Hong, S. Luo, H. S. Duan, H. H. Wang, Y. Liu, G. Li, Y. Yang, *J. Am. Chem. Soc.* **2014**, *136*, 622–625.
- [15] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, S. Il Seok, *Nat. Mater.* **2014**, *13*, 897–903.
- [16] K. Domanski, E. A. Alharbi, A. Hagfeldt, M. Grätzel, W. Tress, *Nat. Energy* **2018**, *3*, 61–67.
- [17] M. Salado, L. Contreras, L. Calio, A. Todinova, C. Lopez-santos, S. Ahmad, A. Borras, J. A. Idigoras, J. A. Anta, *J. Mater. Chem. A* **2017**, *5*, 10917–10927.
- [18] S. Heo, G. Seo, Y. Lee, M. Seol, S. H. Kim, D. Yun, Y. Kim, K. Kim, J. Lee, J. Lee, et al., *Adv. Mater.* **2019**, *1805438*, 1–5.
- [19] M. Salado, L. Calio, L. Contreras-Bernal, J. Idigoras, J. A. Anta, S. Ahmad, S. Kazim, *Materials (Basel)* **2018**, DOI 10.3390/ma11071073.
- [20] G. Grancini, I. Zimmermann, E. Mosconi, D. Martineau, S. Narbey, *Nat. Commun.* **2017**, *8*, 1–8.
- [21] D. J. Kubicki, D. Prochowicz, A. Hofstetter, S. M. Zakeeruddin, M. Grätzel, L. Emsley, *J. Am. Chem. Soc.* **2017**, DOI 10.1021/jacs.7b07223.
- [22] P. Gratia, G. Grancini, J.-N. Audinot, X. Jeanbourquin, E. Mosconi, I. Zimmermann, D. Dowsett, Y. Lee, M. Grätzel, F. De Angelis, et al., *J. Am. Chem. Soc.* **2016**, jacs.6b10049.
- [23] O. Hentz, Z. Zhao, S. Gradečak, *Nano Lett.* **2016**, *16*, 1485–1490.
- [24] J. Schlipf, P. Docampo, C. J. Schaffer, V. Körtgens et al., *J. Phys. Chem. Lett.* **2015**, *6*, 1265–1269.