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# Study of hybrid organic-inorganic halide perovskite solar cells based on MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] absorber layers and their long-term stability.

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## Abstract:

One of the major perovskites used as a light absorber in perovskite solar cells (PSCs) is methylammonium lead iodide (MAPI). MAPI perovskite shows many optimal optoelectronic properties making it a high-performance solar cell material. Nonetheless, PSCs face some limitations related to stability and degradation against moisture, and toxicity due their lead content. The goal of this work is to study the partial substitution of lead iodide (PbI<sub>2</sub>) with the inorganic compound copper iodide (CuI) to enhance the solar cell stability thanks to the hydrophobic properties of the latter. XRD showed a tetragonal crystal structure growth for the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] perovskite films. Even for 20 mol%, CuI was well incorporated into the perovskite lattice structure producing a slight change in the lattice parameters. SEM analysis showed a clear improvement of the film's morphology with the CuI substitution (less pinholes, better uniformity). The optical absorption edges and calculated optical bandgap, around 1.55 eV, remain unchanged with CuI partial substitution. With the increase in CuI/PbI<sub>2</sub> ratio photovoltaic properties of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] devices improved, higher V<sub>OC</sub> and J<sub>SC</sub> are observed. Finally, the stability was studied during 150 days in air and an enhancement of PSCs properties was observed for CuI substituted PbI<sub>2</sub> PSCs.

**Keywords:** Perovskite solar cell; methylammonium lead iodide (MAPbI<sub>3</sub>); substitution; lead iodide (PbI<sub>2</sub>); copper iodide (CuI); long-term stability.

**Declarations:**

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- **Code availability:** Not applicable.
- **Author Contributions:** Conceptualization, Jean-Luc Rehspringer and Aziz Dinia; Formal analysis, Wissal Belayachi; Funding acquisition, Abdelilah Slaoui, Mohammed Abd-Lefdil and Aziz Dinia; Investigation, Wissal Belayachi, Salma Boujmiraz, Salma Zouhair, Kübra Yaşaroğlu and Cédric Leuvrey; Methodology, Kübra Yaşaroğlu, Guy Schmerber, Cédric Leuvrey, Jean-Luc Rehspringer, Thomas Fix and Nicolas Zimmermann; Project administration, Abdelilah Slaoui, Mohammed Abd-Lefdil and Aziz Dinia; Resources, Guy Schmerber, Thomas Fix, Abdelilah Slaoui, Mohammed Abd-Lefdil and Aziz Dinia; Supervision, Kübra Yaşaroğlu, Guy Schmerber, Abdelilah Slaoui, Mohammed Abd-Lefdil and Aziz Dinia; Validation, Jean-Luc Rehspringer, Mohammed Abd-Lefdil and Aziz Dinia; Visualization, Wissal Belayachi; Writing – original draft, Wissal Belayachi; Writing – review & editing, Wissal Belayachi, Kübra Yaşaroğlu, Guy Schmerber, Jean-Luc Rehspringer, Thomas Fix, Abdelilah Slaoui, Mohammed Abd-Lefdil and Aziz Dinia.
- **Ethics approval:** Not applicable.
- **Consent to participate:** Not applicable.
- **Consent to for publication:** Not applicable.

**Relevance Summary:**

The work presented distinguishes itself from past work by its approach. The substitution of the lead component with the inorganic copper iodide was never studied as a mean to improve the stability of the perovskite solar cells. The results presented in this paper show the long-term stability of the perovskite solar cells elaborated and stored in ambient air. The approach and results presented represent this paper's contribution to the advancement of the state-of-the-art.

## 1. Introduction

Organo-lead halide-based perovskite solar cells (PSCs) have long attracted the attention of the scientific community due to the rapid growth of their achievable power conversion efficiency (PCE) [1, 2]. Since the initial report of 3.8% [3], the highest certified PCE of 25.2% [4] was achieved in a decade, making PSCs the fastest advancing solar cell technology to date. PSCs present many advantages such as low-cost and low-temperature fabrication possibilities, available and easily processable raw materials, high open-circuit voltage, bandgap tunability, and large diffusion length of charge carriers [5–7]. The structure of perovskite materials is similar to the mineral calcium titanium oxide, with  $ABX_3$  as chemical formula, where A is an organic, non-organic or hybrid cation, B a metal ion, and X a halide [8]. Among the perovskites used, methylammonium lead halide perovskite ( $CH_3NH_3PbX_3$ ;  $CH_3NH_3 = MA$ ) and its mixed-halide crystals are the most employed and thus have been studied in depth [9–15].

The perovskite films can be elaborated through various deposition techniques [16], from solution-based deposition techniques [17–19] to vapor assisted techniques [20–24]. As for the PSCs devices configuration, multiple device's architectures have been developed such as the mesoporous structure [11, 25, 26], the mesoporous superstructure [12, 27], the planar structure [20, 25], the inverted planar structure [25, 28, 29] and most recently the multijunction configuration [30–32].

However, a major obstacle to the industrialization of the PSCs is the low long-term stability of the devices [33–35]. PSCs are known to degrade by both extrinsic (relative humidity [36–38], temperature [37, 39], oxygen [40] and UV-light [41, 42]) and intrinsic parameters (thermal and electric field induced degradation [43–45], interfacial reactions due to defects or imperfections at grain boundaries [46, 47], corrosion of the contacts by inherent ionic defects in bulk perovskite [34, 44, 45]).

To avoid these problems and to improve the perovskite material as well as the based PV solar cells performances, various tracks have been explored such as mixed halide perovskites [48, 49], mixed-cation [50–52], mixed halide and mixed cation [53], chemical inhibition and passivation [54–57], additives [58–62], the introduction of a buffer or water proof layers [63–65], replacing organic electron/hole transport layers with inorganic materials [66–69].

Another important issue is the toxicity of lead [70], which led researchers to study the metal substitution of the lead compound [71–75]. Most of these reports mention the effects on the characteristics of the devices but not the effects on the long-term stability of the perovskite materials. Among the possible metals, copper has been studied for partial substitution of lead [74, 76] and these studies showed a slight improvement or no improvement at all in the photovoltaic properties of the devices, but none mention the results on the stability of the PSCs. On the other hand, A. Christians et al used copper iodide (CuI) as an inorganic hole conductor material for the organo-lead halide perovskite [66] and the resulting PSCs exhibited stability at high humidity when stored without encapsulation under ambient conditions.

In this paper, our overall goal is to try to improve stability while reducing the toxicity of the materials. We therefore partially substitute lead iodide ( $PbI_2$ ) with the hydrophobic copper iodide (CuI), in the classical methylammonium lead iodide (MAPI or  $MAPbI_3$ ) perovskite. The structural and optical properties of the obtained  $MAI[(PbI_2)_{1-x}(CuI)_x]$  perovskite thin films were investigated as well as the photovoltaic properties of  $MAI[(PbI_2)_{1-x}(CuI)_x]$  based solar cells. The long-term stability of these PSCs under ambient conditions, without use of encapsulation, was also studied.

## 2. Materials and Methods

### 2.1. Materials

Lead iodide ( $\text{PbI}_2$ , 99.999%), copper(I) iodide ( $\text{CuI}$ ,  $\geq 99.995\%$ ), anhydrous dimethylformamide (DMF) ( $\text{HCON}(\text{CH}_3)_2$ , 99.8%), 4-tert-butyl pyridine (4-tBp) ( $\text{C}_9\text{H}_{13}\text{N}$ , 96%), Spiro-MeOTAD ( $\text{C}_{81}\text{H}_{68}\text{N}_4\text{O}_8$ , 99%), anhydrous chlorobenzene ( $\text{C}_6\text{H}_5\text{Cl}$ , 99.8%), and anhydrous acetonitrile ( $\text{CH}_3\text{CN}$ , 99.8%) were purchased from Sigma-Aldrich. Methylammonium iodide (MAI) ( $\text{CH}_5\text{NHI}$ ,  $\geq 98\%$ ) and Lithium Bis(trifluoromethanesulfonyl) (Li-TFSI) ( $\text{C}_2\text{F}_6\text{LiNO}_4\text{S}_2$ , 99.95%) were purchased from Tokyo Chemical Industry (TCI). 2-propanol (IPA) ( $(\text{CH}_3)_2\text{CHOH}$ , 99.5%) was purchased from Carlo Erba. IPA was stored in a bottle containing zeolite sieves to ensure the adsorption of any moisture excess that might be present in the solvent. All the chemicals, other than IPA, were directly used without further purification.

### 2.2. Perovskite and solar cell fabrication

#### 2.2.1. Perovskite thin films preparation

A two-step sequential spin-coating procedure was applied for the synthesis of the perovskite films. The lead precursor solution ( $c = 1 \text{ mol} \times \text{L}^{-1}$ ) was prepared by dissolving  $\text{PbI}_2$  and  $\text{CuI}$ , with a molar ratio of  $x:1-x$  ( $x$  being the  $\text{CuI}$  molar ratio, ranging between 0 and 0.2), in DMF. Then, the solution was heated and stirred on a hot plate at  $70^\circ\text{C}$  for 30 min. For the preparation of the methylammonium precursor solution ( $c = 0.25 \text{ mol} \times \text{L}^{-1}$ ), MAI was dissolved in IPA with the desired molar ratio.

In order to characterize the active layer,  $\text{MAI}[(\text{PbI}_2)_{1-x}(\text{CuI})_x]$  thin films deposited on glass substrates were prepared. First, the lead-copper precursor solutions were spin coated on the glass substrates ( $2 \text{ cm} \times 2 \text{ cm}$ ) at 2000 rpm for 30s, followed by a first annealing at  $70^\circ\text{C}$  for 3 min and a second one at  $90^\circ\text{C}$  for 5 min. In the second step, the methylammonium solution was dropwise deposited on previous film, after a 30s reaction time the excess was removed by spin-coating at 2000 rpm for 30s. The resulting films are then annealed at  $90^\circ\text{C}$  for 30 min in air.

#### 2.2.2. Hole transporting layer solution preparation

First, a lithium solution was prepared by dissolving 0.023 g of Li-TFSI in 45  $\mu\text{L}$  of acetonitrile. Then, 9  $\mu\text{L}$  of the lithium solution, 19.5  $\mu\text{L}$  of 4-tBp and 0.5 mL of chlorobenzene were added to 0.036 g of Spiro-MeOTAD.

#### 2.2.3. Device fabrication

Fluorine-doped tin oxide (FTO) coated glass substrates ( $2 \text{ cm} \times 2 \text{ cm}$ ), coated with a  $\text{TiO}_2$  blocking layer and a scaffolding layer, were purchased from Solaronix company (Switzerland). The substrates were cleaned by sequential ultra-sonication baths in acetone, ethanol, and deionized water for 5 min each. The cleaned substrates were then dried under  $\text{N}_2$  gas flow and treated in a plasma cleaner with oxygen plasma for 3 min to remove the last residual organics. Yellow polyimide tape has been accurately applied to both edges of the front side to ensure that there is no deposition of  $\text{MAI}[(\text{PbI}_2)_{1-x}(\text{CuI})_x]$  on the edges that are reserved for electrical contacts. The  $\text{MAI}[(\text{PbI}_2)_{1-x}(\text{CuI})_x]$  film was deposited on top of the  $\text{TiO}_2$  scaffolding layer by the two-step spin-coating procedure, previously detailed. The hole transporting layer was then deposited by spin

coating at 2000 rpm for 30s. Finally, a 90 nm-thick gold (Au) electrode was deposited by thermal evaporation, under a high vacuum ( $5 \times 10^{-6}$  to  $2 \times 10^{-7}$  Torr), through a shadow mask with an active area of  $0.25 \text{ cm}^2$ .

### 2.3. Characterization

X-ray powder diffraction (XRD) patterns of polycrystalline material were collected using a Bruker-AXS D8 Advance X-ray diffractometer with  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) in the  $2\theta$  range of  $10 - 60^\circ$  with a step size of  $0.02^\circ$  and a time setting of 1s per step. Phase analysis was conducted using XRD software Eva.

Scanning electron microscopy (SEM) was performed using a field emission scanning electron microscope (FSEM JEOL 6700F) coupled with an Energy Dispersive X-ray (EDX) analyzer. The SEM scans were recorded for 15K and 30K magnification and at 5 kV applied voltage. The EDX analyzes were acquired at 7 kV applied voltage.

UV-Vis spectroscopy was carried out using a Perkin-Elmer Lambda 950 spectrophotometer over the spectral range  $200 - 1200 \text{ nm}$ . An integrating sphere was used to collect both, specular and diffuse transmittance to reduce the effect of light scattering originated from refraction and reflection phenomena on the perovskite crystals.

The current density-voltage (J-V) characteristics were recorded with a Keithley 2400 source meter and 300 W collimated Xenon lamp (Newport) calibrated with the light intensity to  $100 \text{ mW.cm}^{-2}$  under AM 1.5 G solar light condition using a certified silicon solar cell. The optical area of the devices measured is  $0.25 \text{ cm}^2$ , and no mask was used during the measurements.

## 3. Results and Discussion

### 3.1. Structure and morphology

#### 3.1.1. X-Ray Diffraction

The XRD pattern of the  $\text{MAI}[(\text{PbI}_2)_{1-x}(\text{CuI})_x]$  films deposited on glass substrates are shown in Fig. 1a. The most intense  $\text{MAPbI}_3$  perovskite characteristic peaks are located at approximately  $14.12^\circ$  and  $28.52^\circ$  ( $2\theta$ ), corresponding to the (110) and (220) lattice planes, respectively. These peaks are observed for our  $\text{MAPbI}_3$  and  $\text{MAI}[(\text{PbI}_2)_{1-x}(\text{CuI})_x]$  ( $0.1 \leq x \leq 0.2$ ) samples. The diffraction peaks profile and values of the  $\text{MAI}[(\text{PbI}_2)_{1-x}(\text{CuI})_x]$  perovskite films are in good agreement with those of the literature as well as with the tetragonal phase of the  $\text{MAPbI}_3$  perovskite (JCPDS file n° 01-083-7582) [77]. No residual CuI or a Cu-based by-product is observed in the detection limit of XRD. For the (001) lattice plane of  $\text{PbI}_2$ , the characteristic peak is still present even with the increase of the CuI doping level. This leads to believe that the  $\text{CH}_3\text{NH}_3\text{I}$  reaction hardly proceeds beyond the surface of the  $\text{PbI}_2$  (or  $\text{PbI}_2\text{-CuI}$ ) films, and that the complete transformation of all the crystalline structure requires a change in the deposition process parameters. A new peak is observed at lower angles ( $11.54^\circ$ ) which might be an indicator to the presence of this complex or a MAPI-based by-product such as observed by Leguy et al [78].

The texture coefficient ( $T_C$ ), which represents the texture of a particular plane, was calculated for each film (Table 1).  $T_C$  of a particular plane is defined by the well-known relation [79] (equation 1):

$$T_C(hkl) = \frac{I(hkl)/I_0(hkl)}{m^{-1} \sum_1^m I(hkl)/I_0(hkl)}, \quad (1)$$

where  $I(hkl)$  is the measured relative intensity of a plane  $(hkl)$ ,  $I_0(hkl)$  the standard intensity of the plane  $(hkl)$  taken from JCPDS data and  $m$  the number of diffraction peaks. The deviation from unity of  $T_C$  implies the preferred growth direction.

**Table 1** Texture coefficient of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] films.

hkl	T <sub>C</sub> [MAPI]	T <sub>C</sub> [MAPI : 10% CuI]	T <sub>C</sub> [MAPI : 20% CuI]
002	0	0	1.8
110	3.1	1.8	1.6
004	0	0.14	3.0
220	3.3	1.5	0.68

For the classic MAPI film, the preferred growth direction is the direction of the (110) plane (Table 1). The same growth direction is found for the MAPI : 10% CuI film. Additionally, the texture coefficient relative to the (002) and (004) lattice planes increased, sign of the emergence of the peaks characteristic of the (002) and (004) lattice planes. Lastly, for MAPI : 20% CuI the growth direction changed over to the direction of the (002) plane, the film's growth direction is now perpendicular to the substrate's surface rather than diagonal.

The crystallite size of MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] films is estimated using the Scherrer formula [80] (equation 2):

$$D = \frac{K\lambda}{\beta \cos(\theta)}, \quad (2)$$

where  $D$  is the average crystallite size perpendicular to the reflecting planes,  $\lambda$  is the X-ray light wavelength,  $\beta$  is the width of the X-ray peak on the  $2\theta$  axis, normally measured as full width at half maximum (FWHM),  $\theta$  is the Bragg angle, and  $K$  is the so-called Scherrer constant.  $K$  depends on the crystallite shape and the size distribution, indices of the diffraction line, and the actual definition used for  $\beta$  whether FWHM or integral breadth [81].  $K$  can have values anywhere from 0.62 and 2.08. In this paper,  $K = 0.94$  was used. In this work, the calculated values of  $D$  represent estimates (discussion on the accuracy of Equation (2) can be found in the literature [82]).

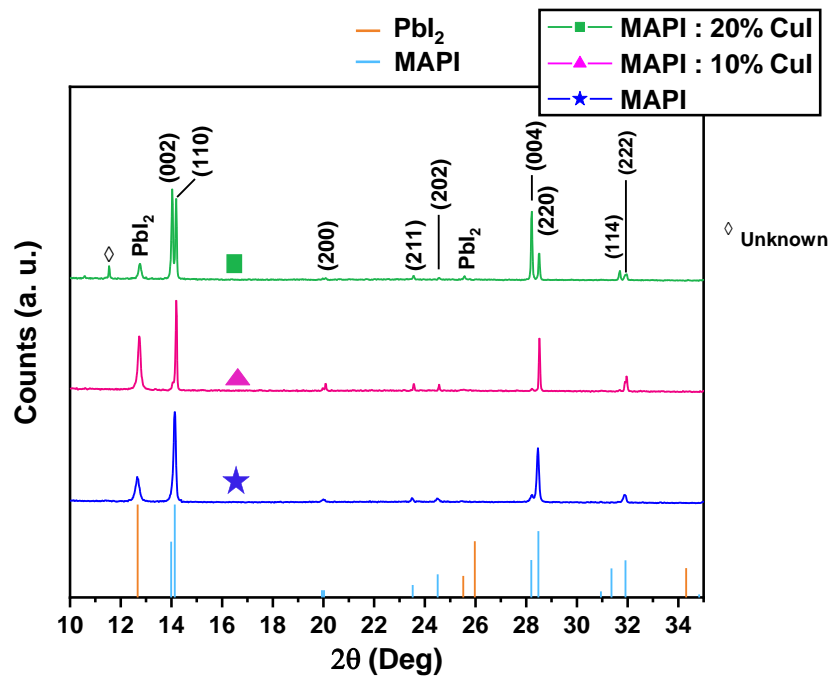
The reported values are an average of the crystallite size determined for the peaks characteristic of the (002), (110), (004) and (220) lattice planes. The crystallite size increases with the introduction of CuI in the lead precursor solution (Table 2).

**Table 2** Estimated cell parameters and crystallite size of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] films.

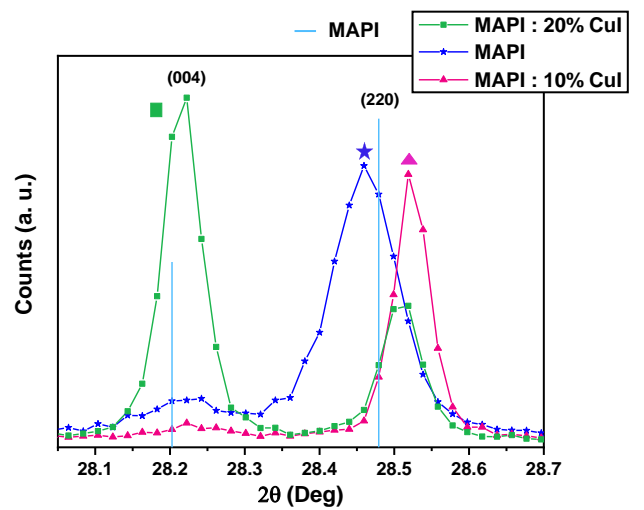
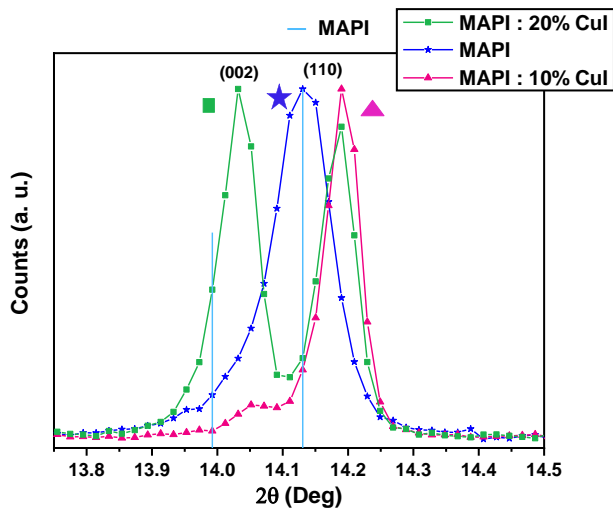
Sample	a=b (Å)	c (Å)	Unit cell volume (Å <sup>3</sup> )	Crystallite Size (nm)
MAPI	8.862 ± 0.004	12.655 ± 0.011	993.8 ± 1.6	79 ± 4
MAPI : 10% CuI	8.841 ± 0.010	12.628 ± 0.014	987.1 ± 3.4	101 ± 8
MAPI : 20% CuI	8.841 ± 0.010	12.633 ± 0.010	987.6 ± 2.9	135 ± 5

To determine the lattice parameters, a refinement of the XRD patterns was carried out using FullProof software, the results are presented in Table 2. It is observed that increasing the CuI doping ratio led to a decrease of the lattice parameter a (respectively the lattice parameter b) and the lattice parameter c. Previous studies demonstrated that the incorporation of ions with smaller ionic radius in MAPbI<sub>3</sub> could reduce the lattice constant [71, 83] thus the change in the lattice parameters is a result of the Pb<sup>2+</sup> ions (119 pm) being partially replaced by the smaller sized Cu<sup>+</sup> ions (73 pm) [72] at the B-sites of the perovskite lattice. However, the absence of change of the lattice parameter a and c between the films containing 10% and 20% of CuI in molar ratio leads to believe that no further substitution of the Pb<sup>2+</sup> ions is taking place.

These results demonstrate that the structure was sensitively affected by the insertion of metal cation in the perovskite structure. When the CuI content is above 10%, the substitution of PbI<sub>2</sub> with CuI results in no changes to the structure.



(a)





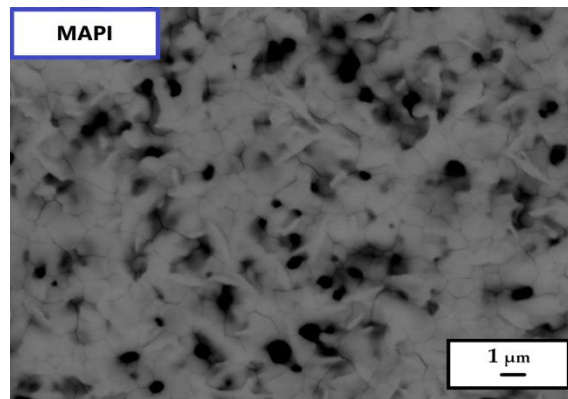
(b)

(c)

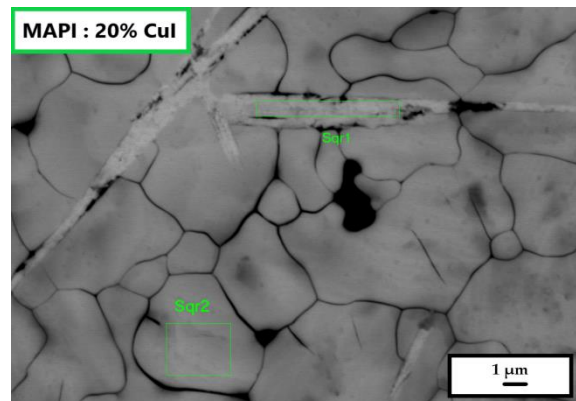
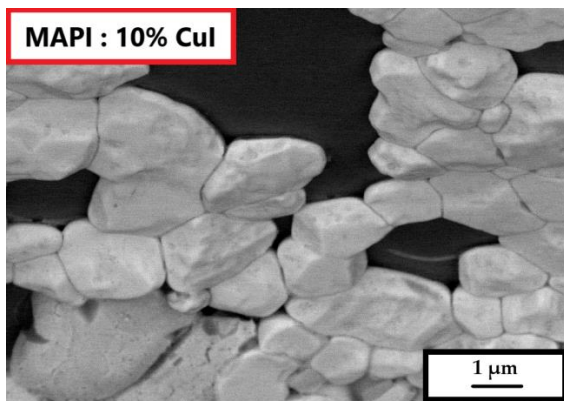
**Fig. 1** (a) X-ray diffraction pattern of MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] films deposited on glass substrates with different CuI incorporation concentrations, (b) a zoom-in of the XRD pattern at (110) lattice plane and (c) a zoom-in of the XRD pattern at (220) lattice plane.

### 3.1.2. SEM characterization

Scanning electronic microscope (SEM) analysis was conducted to investigate the impact of the partial PbI<sub>2</sub> substitution with CuI on the surface morphology. The surface SEM images of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] films deposited on glass substrates are presented in Fig. 2. The pure MAPbI<sub>3</sub> film (Fig. 2a) is composed of densely packed needle-like grains with the domain size distributing in a range of 0.4 - 2 μm, which are composed of smaller crystals based on the crystallite sizes in Table 1. With the addition of CuI, the morphology of the perovskite is improved (Fig. 2b and 2c). The films surface appears to be more homogeneous. The films show more regular shaped grains and a decrease in pinholes density. The grain size also increases with the increase of the CuI/PbI<sub>2</sub> ratio. The grain growth reduces the relative number of pinholes and induces a better surface coverage. Surface between the grains exposed to moisture is reduced which would contribute to improving the long-term stability. Notice that these observations are in good agreement with XRD texture coefficient. Moreover, the perpendicular growth of CuI doped samples could be a less moisture sensitive crystalline orientation.



(a)



(b)

(c)

**Fig. 2 (a-c)** Surface SEM images of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] films deposited on glass substrates.

### 3.2. Optical properties

The absorption spectrum of MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] films deposited on glass substrate are displayed in inset of Fig. 3. The absorption edges span from 740 up to 780 nm.

The incident photon energy ( $h\nu$ ) and  $E_g$  are related through Tauc's equation [84]:

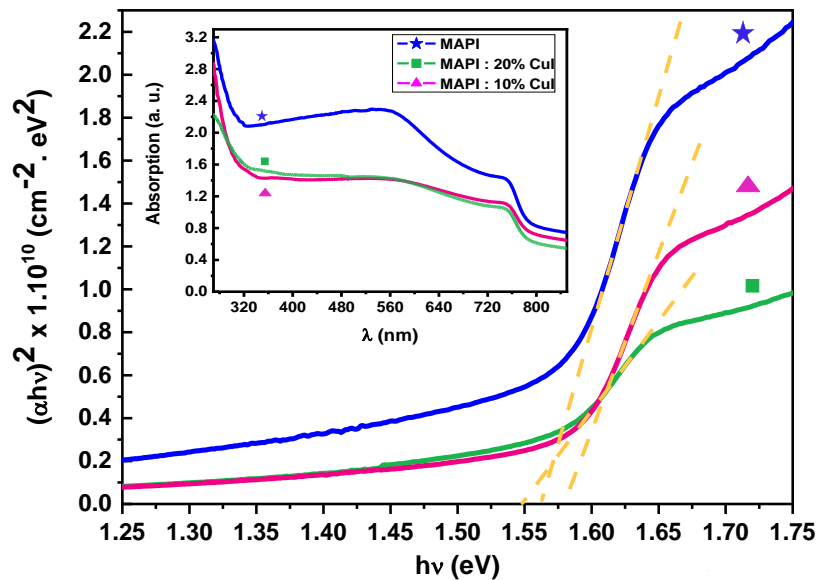
$$(\alpha h\nu) = \beta(h\nu - E_g)^{\frac{1}{n}}, \quad (3)$$

where  $\alpha$  is the absorption coefficient,  $E_g$  the optical bandgap energy,  $\beta$  the constant depending on ( $h\nu$ ) and  $n$  is related to the type of band transition (2 or 1/2 for direct and indirect transitions, respectively). The absorption coefficient  $\alpha$  is calculated through the following relation:

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right), \quad (4)$$

where  $T$  is the optical transmission and  $d$  the thickness of the sample.  $d$  is estimated to be around 330 nm (determined by profilometric analysis).

In the assumption of a direct band transition for the tetragonal MAPbI<sub>3</sub> perovskite [26, 85], the optical bandgap ( $E_g$ ) of the samples was estimated by extrapolating the linear part of Tauc's plots ( $(\alpha h\nu)^2$  vs. ( $h\nu$ )) that intercepts the energy axis (Fig. 3). The estimated bandgap of MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] are  $1.56 \pm 0.05$  eV for MAPbI<sub>3</sub>,  $1.55 \pm 0.05$  eV for MAPI : 10% CuI and  $1.58 \pm 0.05$  eV for MAPI : 20% CuI. The estimated  $E_g$  are in agreement with the reported value for tetragonal MAPbI<sub>3</sub> perovskite (1.55 eV) [10, 85] and are barely affected by the change in CuI fraction. It also remains close to the optimal band gap for photovoltaic performance (1.4 eV).



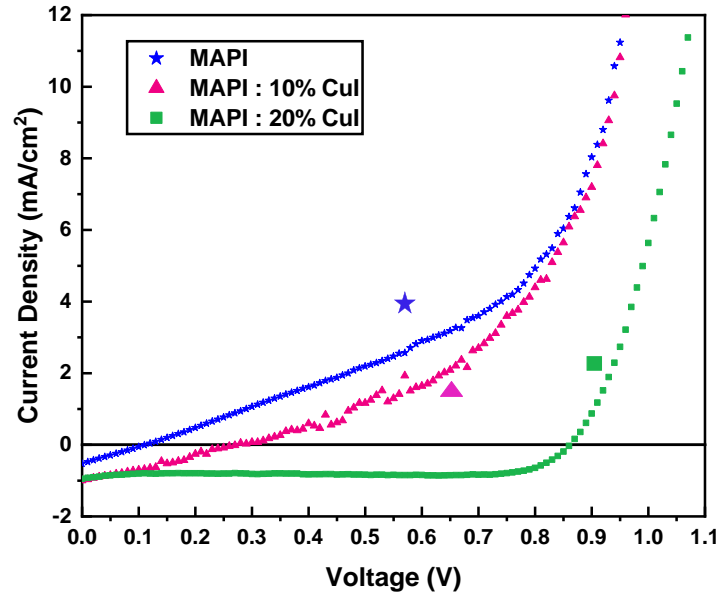
**Fig. 3.** UV - Visible absorption spectra of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] films and Tauc's plots show a slight variation in optical bandgap of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] films.

### 3.3. Photovoltaic devices

#### 3.3.1. Performance

The current density–voltage (J–V) characteristics for the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] based photovoltaic devices are shown in Fig. 4, and the photovoltaic characteristics are listed in Table 3. Overall, the various devices presented low photovoltaic performance compared to the literature.

For the MAPbI<sub>3</sub> device, the very low photovoltaic performances are attributed to the existence of pinholes, as observed in Fig. 2. The pinholes compromise the efficiency by introducing shunt paths in the device. When Pb<sup>2+</sup> is substituted with Cu<sup>+</sup>, the photovoltaic characteristics are slightly improved, except for the short circuit current density (J<sub>sc</sub>) and series resistance (R<sub>s</sub>). Indeed, for the MAPI : 20% device the fill factor (FF) increases from 23.4 up to 69.1 %, and the open circuit voltage (V<sub>oc</sub>) from 120.1 up to 869 mV. Consequently, a slight enhancement of power conversion efficiency (PCE) is observed. Furthermore, the MAPI : 20% device exhibits the largest shunt resistance (R<sub>sh</sub>), an indicator of the lessening of shunt paths in the device (reduction of pinholes), as witnessed by the higher FF and V<sub>oc</sub>. The results are promising and show an effect of the partial substitution of PbI<sub>2</sub> by CuI, which was not the case in the work reported by Frolova et al. They found that there is no benefit to the substitution of Pb<sup>2+</sup> with monovalent ions, such as Cu<sup>+</sup> or Ag<sup>+</sup> [74].



**Fig. 4** Photocurrent-Voltage (J-V) characteristics of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] based photovoltaic devices.

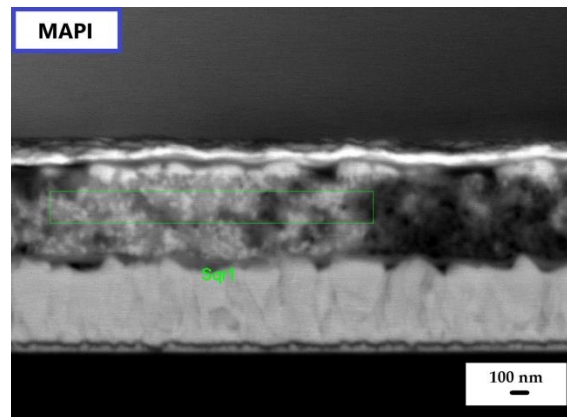
**Table 3** Photovoltaic characteristics of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] based photovoltaic devices

	MAPI	MAPI : 10% CuI	MAPI : 20% CuI
J <sub>sc</sub> (mA/cm <sup>2</sup> )	0.53	1.0	0.95

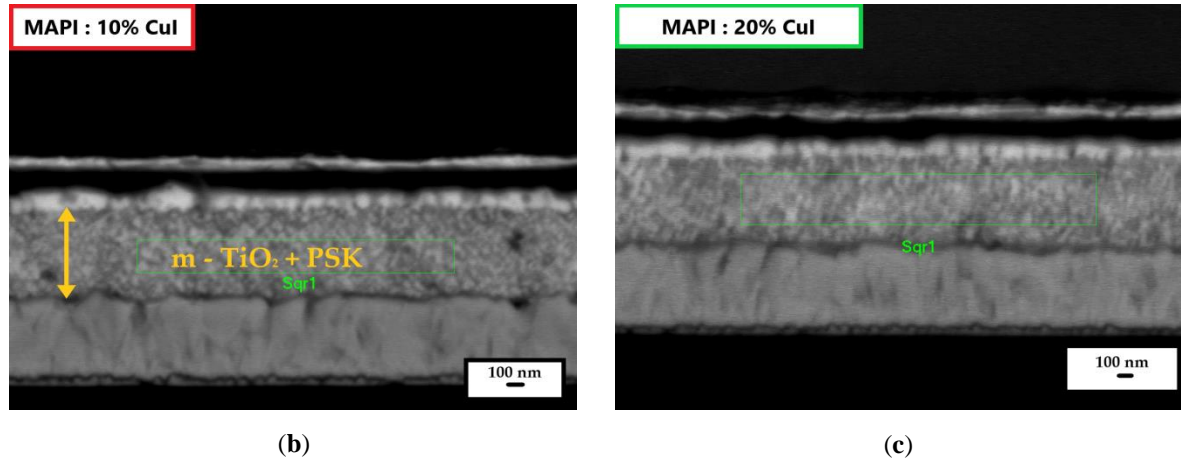
$V_{oc}$ (mV)	120	275	864
FF (%)	23.4	29.5	69.1
PCE (%)	0.02	0.08	0.57
$R_{sh}$ ( $\Omega.cm^2$ )	$178 \pm 4$	$196 \pm 12$	$8736 \pm 559$
$R_s$ ( $\Omega.cm^2$ )	$11.9 \pm 0.1$	$15.6 \pm 0.2$	$44 \pm 2$

### 3.3.3. SEM and EDX analysis

The cross-sectional SEM images of the complete MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] based photovoltaic devices with glass/ FTO/TiO<sub>2</sub> compact layer/ mesoporous TiO<sub>2</sub>/perovskite/ spiro-OMeTAD/Au are shown in Fig. 5. One can clearly see that the partial substitution of PbI<sub>2</sub> with CuI has a strong impact on the structure of the solar cells. Indeed, a better pore-filling within the mesoporous TiO<sub>2</sub> scaffold is observed with the increase of CuI/PbI<sub>2</sub> ratio. This improvement in pore filling induces an expansion of the contact area between the perovskite and TiO<sub>2</sub> improving therefore carrier exchange and transport. Additionally, the thickness of the layer of non-infiltrated perovskite, or overlayer, decreases with the increase of CuI content. The thickness of the overlayer went from approximatively 200 nm for the MAPbI<sub>3</sub> device to 145 nm for the MAPI : 10% CuI device and 115 nm for the MAPI : 20% CuI device. The spiro-OMeTAD layer and gold contact are also better deposited with the increase of CuI/PbI<sub>2</sub> ratio. The increased FF and  $V_{oc}$  for the MAPI : 20% CuI maybe due to the better pore-filling within the mesoporous TiO<sub>2</sub> scaffold compared to the imperfect pore-filling for the MAPbI<sub>3</sub> device. It must be kept in mind that TiO<sub>2</sub> mesoporous layer has been heat sintered at 500°C and this leads to a bad wettability by DMF. Addition of CuI seems to contribute to a better compatibility between the lead precursor solutions and TiO<sub>2</sub> surface. EDX analysis was carried out on the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] based photovoltaic devices and it showed that the intensity of the peaks corresponding to the elements constituting the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] perovskite increases with the increase of CuI fraction, which is proof of the better pore-filling within the mesoporous TiO<sub>2</sub> scaffold with the increase of CuI fraction. Nonetheless, the low  $J_{sc}$  suggests still an insufficient contact area within the mesoporous TiO<sub>2</sub> scaffold. Notice that the preparation technique, the two-step process, could be an objective reason for those low efficiencies. As on glass surface the penetration of MAI is certainly weak and a PbI<sub>2</sub> grabbed layer remains impinging the carrier collection.



(a)

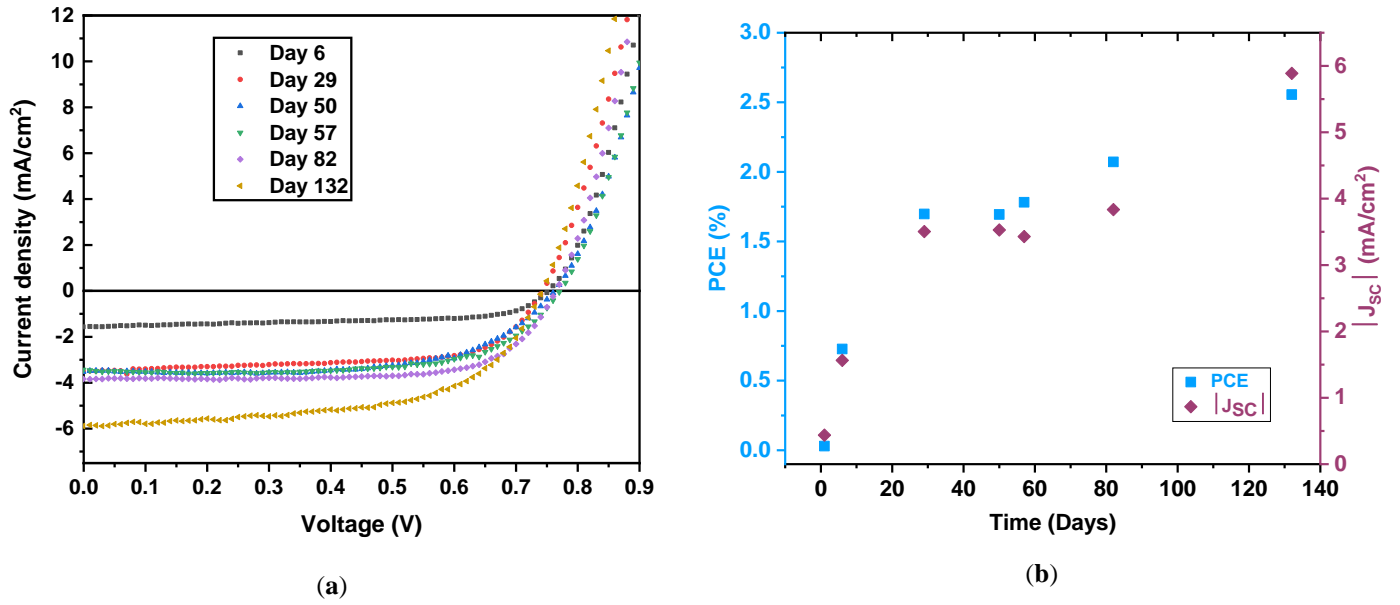


**Fig. 5 (a-c)** Cross-sectional SEM images of complete MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] based photovoltaic devices.

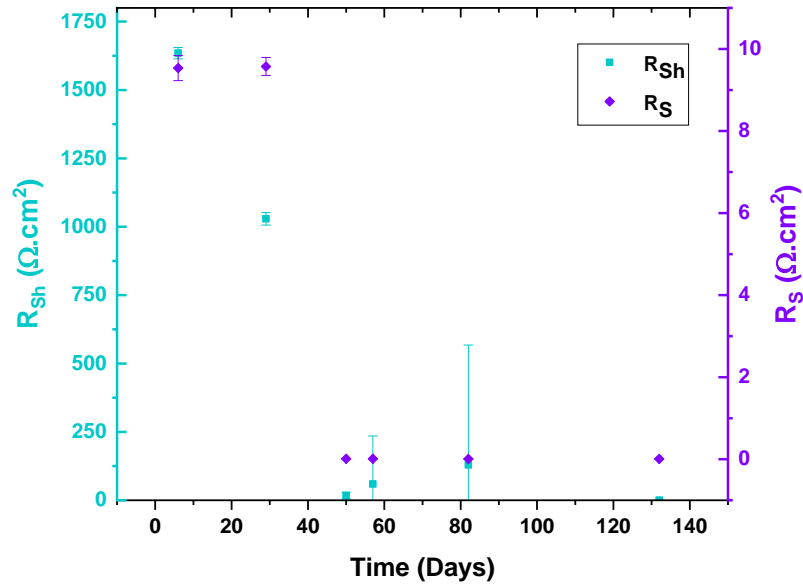
### 3.3.3. Long-term stability

The evolution of the (J-V) characteristic, the  $J_{SC}$  and the PCE of the MAPI: 10% CuI based photovoltaic device as a function of time are displayed in Fig. 6, and the evolution of  $R_{Sh}$  and  $R_S$  are reported in Fig. 7. The device was stored in dark at room temperature without encapsulation. The solar cell was characterized for over four months. As previously reported, the MAPbI<sub>3</sub> perovskite solar cells are unstable in ambient air [26–28]. In our case, the initial PCE improved with time (Fig. 6b). The appearance of the (J-V) characteristic and the evolution (following an exponential) of the PCE indicate that both the PCE and stability of the device in ambient air are improved after the substitution of Pb<sup>2+</sup> with Cu<sup>+</sup>. The decrease of the  $R_S$  ( $8 \times 10^{-3} \pm 2 \times 10^{-4} \Omega \cdot \text{cm}^2$  for day 132) is consistent with the increase of the  $J_{SC}$  (Fig. 7). However, the decrease of  $R_{Sh}$  is detrimental to any further improvement of the FF or  $V_{OC}$ . Furthermore, no change in color in the perovskite film was observed until the beginning of the fifth month. The MAPI : 10% CuI based photovoltaic device started to deteriorate due to the degradation of the perovskite layer (yellowing of the layer).

One explanation of the favorable evolution could be found in the evolution of transversal composition. It seems like a latent kinetic reaction, which improves the contact areas between the perovskite layer and the other layers, takes place over time. As detected in the layers deposited on glass substrate, after ending the two-step process a PbI<sub>2</sub> grabbed layer is observed. In solar cells prepared with the same two-step process we assigned the poor  $J_{SC}$  to a grabbed PbI<sub>2</sub> layer that limits the carrier collection. Due to mobility of methylammonium a homogenization of the present phases can occur along the time and the amount of photosensitive phase in contact with p and n layer increases leading to an improvement of cell performance and long-term stability.



**Fig. 6** Evolution of (a) the (J-V) characteristic and (b) the JSC and the PCE of the MAPI : 10% CuI based photovoltaic device as a function of time after storage in dark in ambient environment at room temperature without encapsulation.



**Fig. 7** : Evolution of the resistances of the MAPI : 10% CuI based photovoltaic devices as a function of time after storage in dark in ambient environment at room temperature without encapsulation.

#### 4. Conclusions

In summary, we have studied the partial substitution of PbI<sub>2</sub> with CuI into the solution-processed MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] perovskite films. XRD analysis showed that the diffraction pattern of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] perovskite thin films fit with the tetragonal MAPbI<sub>3</sub> perovskite structure but residual PbI<sub>2</sub> was detected. Up to 10% doping ratio no impurity or by-products of CuI were observed which seems to indicate the optimum ratio for Cu incorporation in the MAPbI<sub>3</sub> lattice is 10%. SEM analysis images of the

MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] perovskite thin films showed that the film homogeneity was improved, and the grain size was enhanced with the increase of CuI/PbI<sub>2</sub> ratio. The estimated optical band gaps were in agreement with the reported value for tetragonal MAPbI<sub>3</sub> perovskite (1.55 eV) and remains unaffected by the partial substitution of PbI<sub>2</sub> with CuI.

MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] based photovoltaic devices fabricated by spin-coating method clearly demonstrates the effect of the partial substitution of PbI<sub>2</sub> with CuI on the photovoltaic properties. V<sub>OC</sub>, FF and PCE improved with the increase of CuI/PbI<sub>2</sub> ratio. The improvement of these photovoltaic parameters might be due to the better pore-filling of perovskite with the addition of CuI observed through SEM analysis. However, the J<sub>SC</sub> remains low for all devices. Nonetheless, the long-term stability of the MAI[(PbI<sub>2</sub>)<sub>1-x</sub>(CuI)<sub>x</sub>] based photovoltaic devices was improved with the partial substitution of PbI<sub>2</sub> with CuI.

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