DROP-IT

DELIVERABLE 2.3

Inkjet-printed films of B-LFPs from molecular precursors on a flexible substrate

Due date of deliverable: 2020/10/31

Actual submission date: 2020/12/22

Deliverable number:	D2.3
Due date:	2020/10/31
Nature[1]:	R
Dissemination Level[1]:	PU
Work Package:	WP2
Lead Beneficiary:	UB
Contributing Beneficiaries:	SRI

[1] **Nature:** R = Report, P = Prototype, D = Demonstrator, O = Other
Dissemination level PU = Public PP = Restricted to other programme participants (including the Commission Services) RE = Restricted to a group specified by the consortium (including the Commission Services) CO = Confidential, only for members of the consortium (including the Commission Services) Restraint UE = Classified with the classification level "Restraint UE" according to Commission Deci-sion 2001/844 and amendments Confidential UE = Classified with the mention of the classification level "Confidential UE" according to Commission Decision 2001/844 and amendments Secret UE = Classified with the mention of the classification level "Secret UE" according to Commis-sion Decision 2001/844 and amendments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

DOCUMENT HISTORY

Version	*Date*	*Reason of change*
1	2020/12/15	SRI contribution
2	2020/12/17	SRI revision
3	2020/12/22	General revision by UVEG and approval
4		

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

Table of Content

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

1 Introduction

Drop-it project attempts to revolutionize photovoltaics and optoelectronics by combining the extraordinary properties of thin film perovskites (lead-free) and solution processed large area deposition methods like drop on demand inkjet technology. During the timeline of DROP-IT we will validate materials and technologies by fabricating high performance, stable and cost-effective solar cells, LEDs and active photonic waveguides. Furthermore, we plan to develop those devices on top of flexible substrates (deliverable 2.1 addresses the selection of the best available flexible substrates). The perovskites to be used with inkjet technology must be formulated either from nanoparticulate colloidal suspensions or precursors. This deliverable reports on the processing of lead-free perovskite and rudorffite thin films for benchmarking purposes (B-LFPs), even if rudorffites can be considered also as a first generation of lead-free perovskite-like (or perovskitoid) materials.

The main objective of this deliverable is focused on demonstrating inkjet printing technology as a powerful tool for the upcoming flexible printed optoelectronics devices based on B-LFPs. Indeed, in this work, the inkjet printing technology is validated as a versatile method for the deposition of different functional inks based on B-LFPs. Inkjet-printing technology would contribute to change paradigms by improving several drawbacks of more traditional lithography intensive technologies. Drop on demand inkjet technologies promise improving the manufacturing processes (customized prototype within an inline and roll-to-roll manufacturing) and the development of novel PV and LED devices on flexible substrates with a low-cost investment.

This deliverable 2.3 reports the achievements on inkjet printed B-LFPs thin films deposited on flexible substrates, starting from molecular precursors.

2 Results

2.1 Inkjet printing of $FASnI_3$ thin films from molecular precursors on flexibles substrate in ambient environment

$FASnI_3$ thin films were inkjet printed on flexible PET/ITO/PEDOT:PSS substrates using Dimatix Materials Printer DMP-2850 equipment, located and operated inside a fume hood in ambient environment. The precursor ink was prepared using commercially available precursors inside a nitrogen filled glovebox with well controlled oxygen and humidity levels below 1 ppm. In order to protect the precursor ink from oxidation (Sn^{2+} → Sn^{4+}) during handling and printing, an inert protecting agent was added on top of the precursor ink. The recipe for the $FASnI_3$ composition was adopted from Jiang et al. [1] and modified to meet the inkjet printing requirements. In particular, it was important to reduce the concentration of the precursor ink to enable inkjet printing and achieve a submicron thick film. Although the printing step could be achieved in ambient environment without visible degradation of the precursor ink, post deposition thermal annealing in air did not result in the formation of the target $FASnI_3$ thin films due to the presence of oxygen and humidity. To achieve successful $FASnI_3$ formation post printing, a vacuum assisted annealing step was introduced to protect the wet layer from oxygen and humidity during the crystallization process. A schematic illustration of the individual steps is shown in Figure 1.

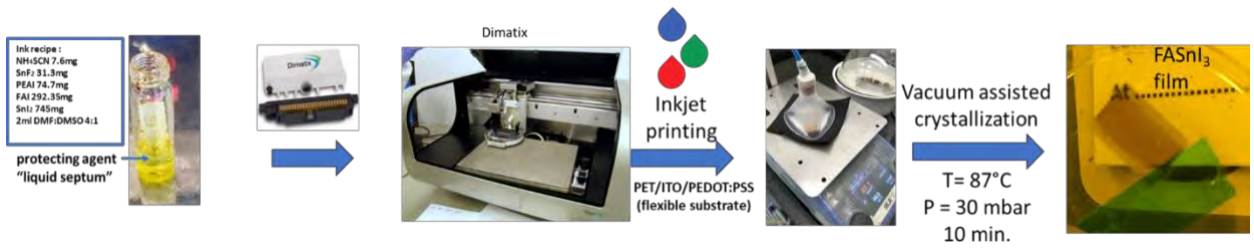

Figure 1. Schematic of individual steps involved in inkjet printing of $FASnI_3$ thin films in ambient environment.

The obtained thin film through inkjet printing and subsequent vacuum assisted crystallization approach displayed the characteristic brownish-dark colour as expected for $FASnI_3$ thin films, indicating a successful perovskite formation. However, the SEM analysis (Figure 2, left) showed a poor morphology and uniformity along with many pinholes throughout the entire measured area of the sample (Figure 2). In spite of this, the XRD pattern confirmed the presence of the target $FASnI_3$ material. The most intense $FASnI_3$ Bragg peak for the (100) plane was detected at 14.37° (2-theta). However, the XRD analysis also indicated the presence of significant amounts of undesired byproduct(s) or unconverted precursors. In fact, the intensity of the non-perovskite diffraction peak observed at 12.51° (2-theta) was much more intense in comparison to the diffraction peak of the $FASnI_3$ material, as observed in Figure 2 (right).

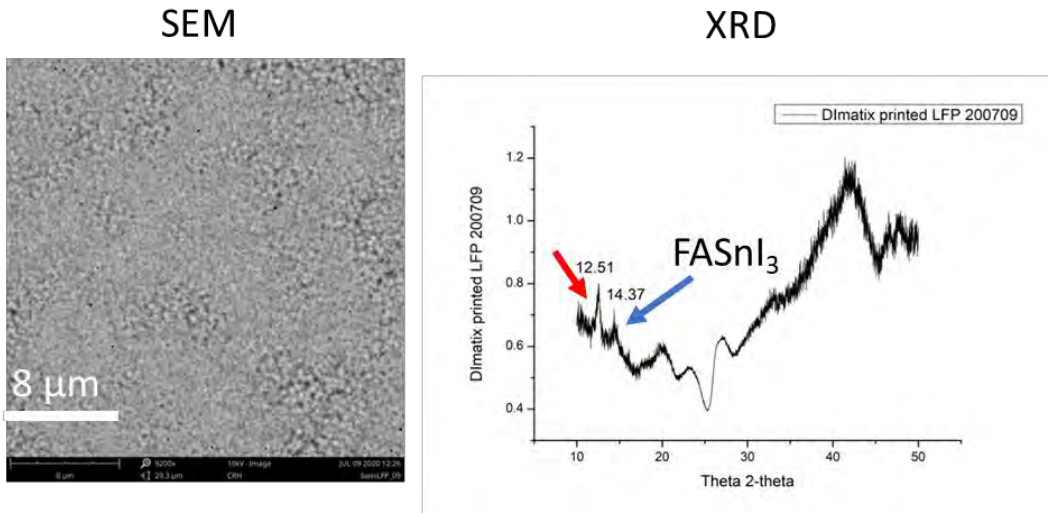

Figure 2. Inkjet printed $FASnI_3$ thin film in ambient conditions and crystallized using vacuum assisted annealing process on a flexible PET/ITO/PEDOT:PSS substrate: (left) SEM image and (right) XRD pattern. Blue arrow indicates the diffraction peak of the (100) plane for $FASnI_3$, while the red arrow indicates the signal from some byproduct.

2.2 Inkjet printing of Ag_3BiI_6 thin films on flexibles substrate in ambient environment, starting from molecular precursors

Ag_3BiI_6 thin films were inkjet printed on flexible PET/ITO/PEDOT:PSS substrates using the same Dimatix Materials Printer DMP-2850 equipment as in precedent section, located and operated inside a fume hood in ambient environment. The precursor ink was prepared using commercially available molecular precursors (AgI and BiI_3) inside a nitrogen filled glovebox with well controlled oxygen and humidity levels below 1 ppm. 4 ml of anhydrous DMSO solvent were added to 3 equivalents of AgI (purity 99.999%) and one equivalent of BiI_3 (purity 99%) powders and stirred for 30 minutes at 60 °C until a clear orange precursor ink (20 wt%) was obtained. The resulting Ag_3BiI_6 precursor ink was found to be stable in ambient environment and therefore could be transferred to the printing cartridge without additional measures. The inkjet printing of the precursor ink (left panel in Figure 3) on flexible PET/ITO/PEDOT:PSS substrates resulted in a yellow wet film (central panel in Figure 3) that turned dark upon annealing in air at 100 °C for 10 minutes, as shown in Figure 3 (right panel).

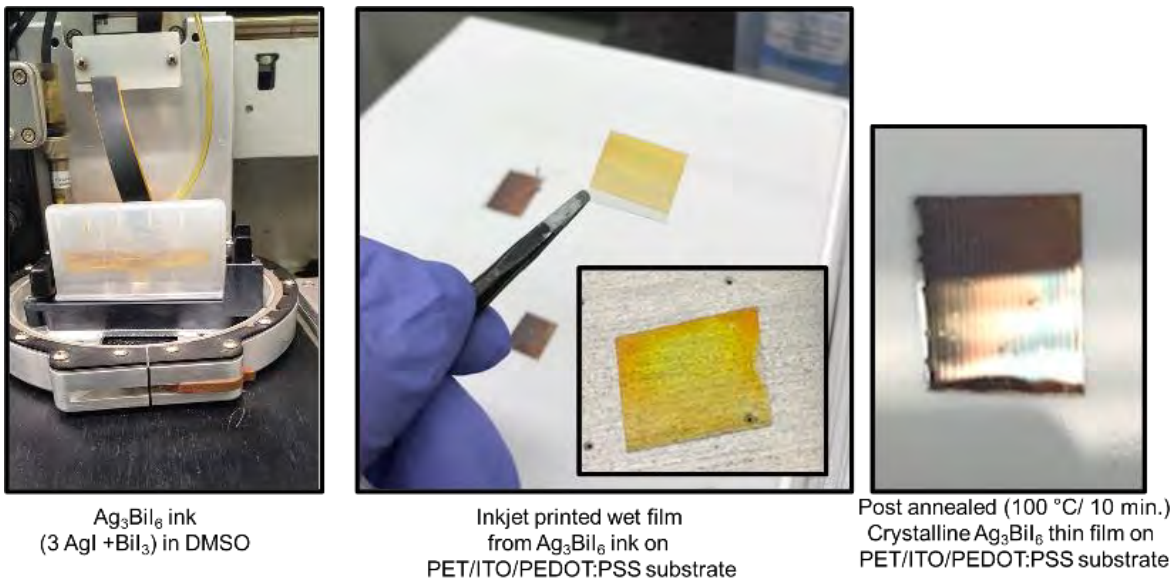

Figure 3 (left) Ag_3BiI_6 precursor ink filled into DIMATIX cartridge. (middle) Inkjet printed wet film from Ag_3BiI_6 precursor ink on PET/ITO/PEDOT:PSS substrate.

The XRD pattern and the absorption spectrum of the post annealed Ag_3BiI_6 thin films is depicted in Figure 4. The characteristic diffraction peak observed at 12.80° (2-theta) assigned to the (111) plane of Ag_3BiI_6 indicates the successful formation of the target rudorffite thin film. The recorded UV-Vis spectrum matches well with literature reports for spin-coated Ag_3BiI_6 thin films [2], and also with the absorption spectra measured for films made of Ag_3BiI_6 nanocrystals synthesized by Avantama, as reported in Deliverable D1.3. From the absorption onset we estimate the band gap energy to be around 1.7 eV, also in good agreement with literature reports [2].

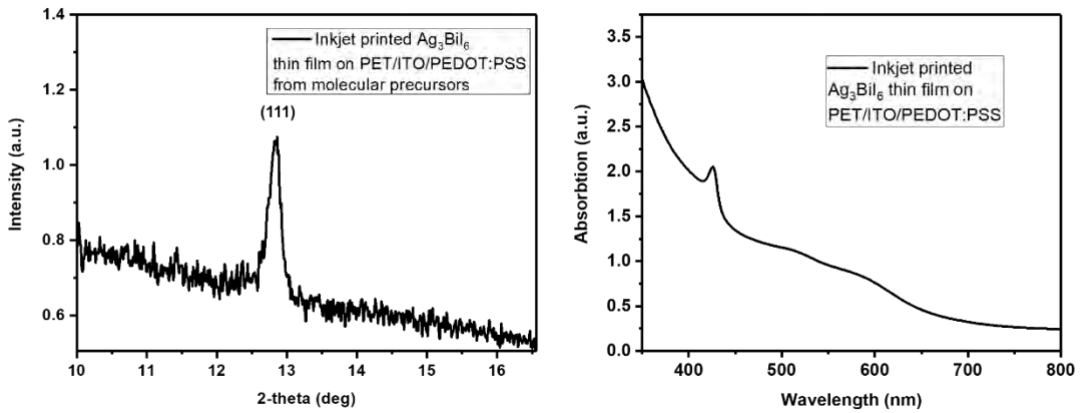

Figure 4. (left) XRD pattern of inkjet printed Ag_3BiI_6 thin film on flexible PET/ITO/PEDOT:PSS substrate. (right) absorption spectrum of Ag_3BiI_6 thin film on flexible PET/ITO/PEDOT:PSS substrate.

The surface morphology and topography of the thin film was studied using SEM and AFM techniques, the resulting SEM and AFM images are shown in Figure 5. From the SEM and AFM images it is evident that the inkjet printed films are pinhole free and uniform on the micron scale, although the root mean square roughness value of 53.13 nm derived from AFM measurements indicates that the obtained layer is rather rough and it should be improved in the future.

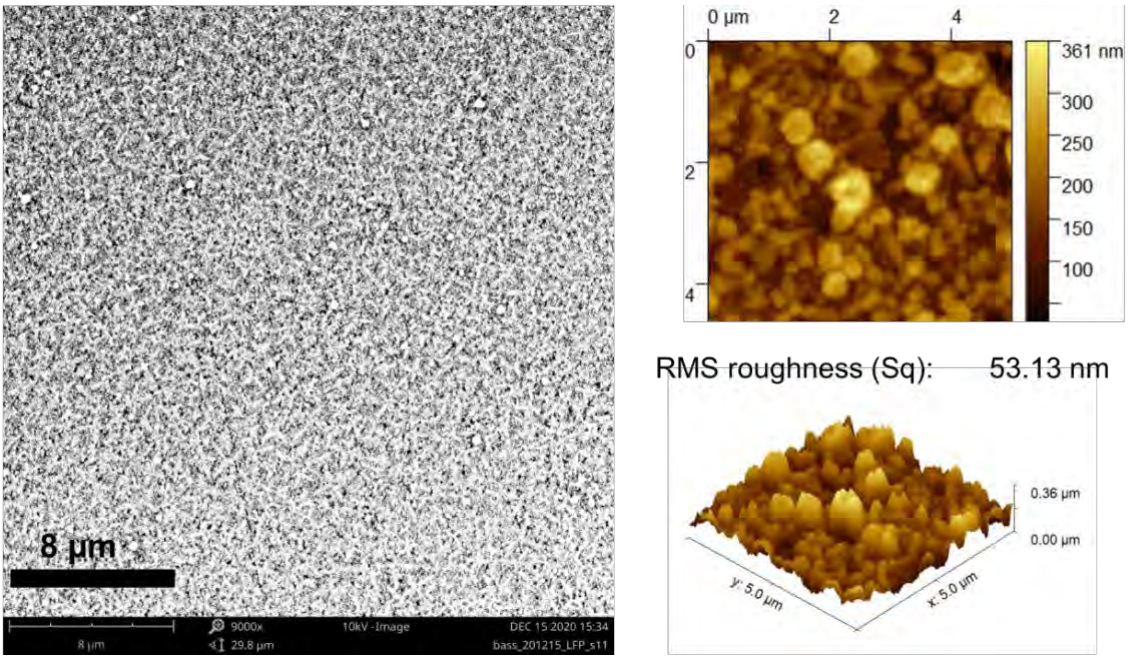

Figure 4. (left) SEM image of inkjet printed Ag_3BiI_6 thin film. (right) 2D and 3D AFM topography images of printed Ag_3BiI_6 thin film.

3 Conclusions & Future directions

Inkjet printing of Sn2+ based perovskites in air is not promising due to ink degradation, even if this step was solved by a novel developed “septum liquid” that protects the solution in ambient conditions. The inkjet printed films were annealed using vacuum assisted processing, but some extra phase was detected by XRD. The best solution would be the use of the Inkjet printer inside a glovebox.

To the best of our knowledge Inkjet printing of (silver-bismuth-halide rudorffites, in general) **Ag_3BiI_6 was demonstrated for the first time within DROP-IT project!** In future experiments, other compositions, as $AgBiI_4$, Ag_2BiI_5, $AgBiI_7$, etc., will be printed and do full characterization to identify which compound works best for the flexible substrate (annealing temperature/time) and with our selected set of charge transport materials (Deliverable D2.2).

In summary, silver-bismuth-halide rudorffites were synthesized by inkjet printing from molecular precursors under ambient conditions (inks prepared in glove box) and the resulting films were stable. This is a big advantage that was preconized in our project application. Therefore, this G-LFP family will be further studied and eventually used as benchmark-LFP for developing solar cells, in the meantime a glove box is acquired and an inkjet printer installed inside. Another parallel action can be the optimization of films and PV devices (WP3) prepared by the already installed doctor blading technique inside a glove box.

References

[1] Jiang, X.; Wang, F.; Wei, Q.; Li, H.; Shang, Y.; Zhou, W.; Wang, C.; Cheng, P.; Chen, Q.; Chen, L.; Ning, Z., Ultra-high open-circuit voltage of tin perovskite solar cells via an electron transporting layer design. *Nature Communications* **2020,** *11* (1).

[2] Ivan, T.; Said, K.; Eisuke, I.; Toshiyuki, U.; Koji, Y.; Hiroshi, T.; Hideo, Y.; Michio, K.; Shinji, A., Photovoltaic Rudorffites: Lead-Free Silver Bismuth Halides Alternative to Hybrid Lead Halide Perovskites. *ChemSusChem* **2017,** *10* (19), 3754-3759.