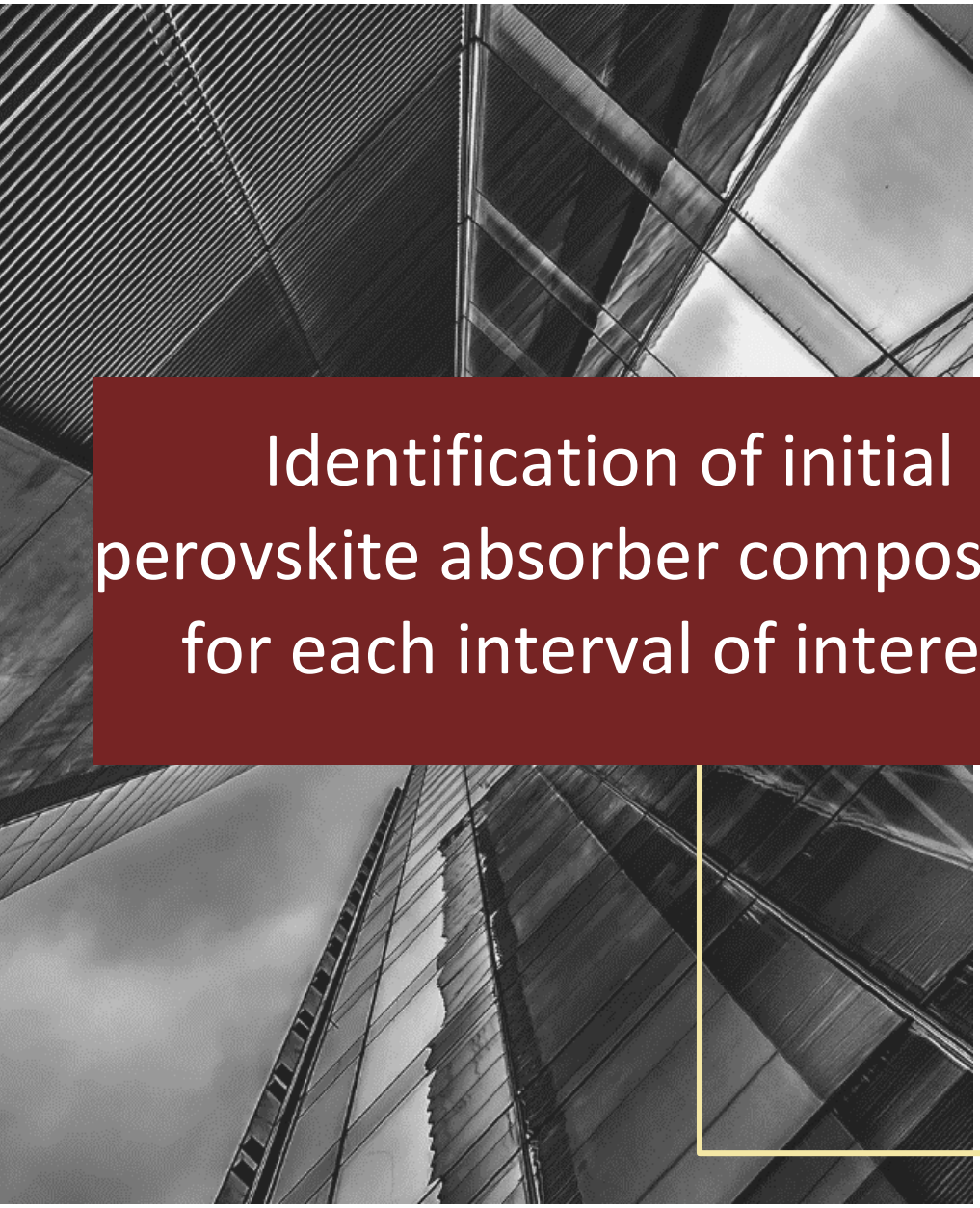
VALHALLA

DELIVERABLE REPORT



Identification of initial perovskite absorber composition for each interval of interest

Deliverable D1.1
June-2023

PREPARED BY
IIT, UOX, UVEG
COORDINATED BY
UVEG

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VALHALLA aims to develop perovskite solar cells and modules with power conversion efficiencies above 26 % (modules > 23 %) and extrapolated operational lifetime > 25 years, following an eco-design approach: employing harmful-solvent-free perovskite deposition, optimized use of materials, circularity, recyclability, scalable and low-cost manufacturing processes, to create a viable economic pathway for the European commercialization of this sustainable technology.

VALHALLA is formed by a multi-disciplinary consortium: 12 partners from 8 European countries; 3 industrial partners & 9 RTOs, covering the whole value chain of innovation from research centres to technology providers, end-users and market and policies.

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VALHALLA Consortium

Organization name	Short name	Country
UNIVERSITAT DE VALENCIA	UVEG	ES
KAUNO TECHNOLOGIJOS UNIVERSITETAS	KTU	LT
RIJKSUNIVERSITEIT GRONINGEN	RUG	NL
CONSIGLIO NAZIONALE DELLE RICERCHE	CNR	IT
FONDAZIONE ISTITUTO ITALIANO DI TECNOLOGIA	IIT	IT
UNIVERSITE DE LIEGE	ULiège	BE
THE CHANCELLOR, MASTERS AND SCHOLARS OF THE UNIVERSITY OF OXFORD	UOXF	UK
ENEL GREEN POWER SPA	EGP	IT
TEKNOLOGIAN TUTKIMUSKESKUS VTT OY	VTT	FI
ICARES CONSULTING	BI	BE
ARK METRICA LTD	ARKM	UK
CSEM CENTRE SUISSE D'ELECTRONIQUE ET DE MICROTECHNIQUE SA - RECHERCHE ET DEVELOPPEMENT	CSEM	CH

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Abbreviations and acronyms list

Abbreviation	Meaning	Abbreviation	Meaning
PCE	Power conversion efficiency	CS	Cesium
FA	Formamidinium	XRD	X-ray Diffraction
PV	Photovoltaic	LED	Light emitting diode
MA	Methylammonium	T	Temperature

1. Executive Summary

Valhalla has identified three main spectral intervals of interest for the development of stable and efficient single junction perovskite solar cells. Thus, perovskites thin films with different bandgaps (Eg) must be developed through vapor deposition, through the tuning of the chemical composition of the perovskite 's crystalline unit. During the first six months of Valhalla, based on observations collected from the behaviour of compounds in devices, and from preliminary stability tests, we have decided to proceed our research on the following perovskites' compositions. 1) $FAPbI_3$ (mid spectral range, about 1.55 eV band-gap), the compound which has currently demonstrated the highest PCE in the literature (> 25%); 2) $Cs_yFA_{1-y}PbSnI_3$ (low spectral range, < 1.4 eV band gap), the compound with the bandgap closer to the ideal one for efficient absorption of the solar spectrum; 3)) $Cs_yFA_{1-y}Pb(I_xBr_{1-x})$ (>1.8 from Oxford) to meet the requirements for the realization of PV devices for indoor applications.

These choices will be monitored for the next six months, in light of results obtained from further tests in complete device structures. Then, the selection of first materials set for efficient and stable solar cells is expected for the Milestone 4.

1.1. Description of the deliverable content and purpose

The selection of compounds has been mainly based on the observation of the behaviour of thin films once embodied in devices and on the analysis of preliminary stability data, collected on thin films.
Regarding the aging tests, an ageing protocol has been agreed which will be used not only for the thin films studies, but also for the analysis of the complete stack of different layers making the full diode structure. In details it includes the recording of XRD patterns, UV-vis and photoluminescence spectra over time upon the exposure of the thin films to the following conditions:

- Dark, T = at 25°C and 85°C, in inert atmosphere
- Under light (light soaking with LED solar simulator, 1 sun), T = 25°C and 85°C, in inert atmosphere

Different chemical compositions and different nominal stoichiometry have been tested at UVEG, UOXF, and IIT.

- **Mid- range bandgap perovskites, i.e 1.5 < Eg < 1.7.** Compounds developed in this range are those currently delivering the highest power conversion efficiency once embodied in a device. In such direction, $FAPbI_3$ must necessarily be the starting composition, providing the lowest

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bandgap. However, it is notorious its phase instability, thus two promising compositions have been selected to stabilize the phase. One is based on the simple introduction of a small amount (<< 50%) of methylammonium cation, $FA_yMA_{1-y}PbI_3$. One is based on the introduction of a small amount of Cs cation and Cl anion doping, nominally $\mathbf{Cs_{15}FA_{85}Pb(I_xCl_{1-x})_3}$.

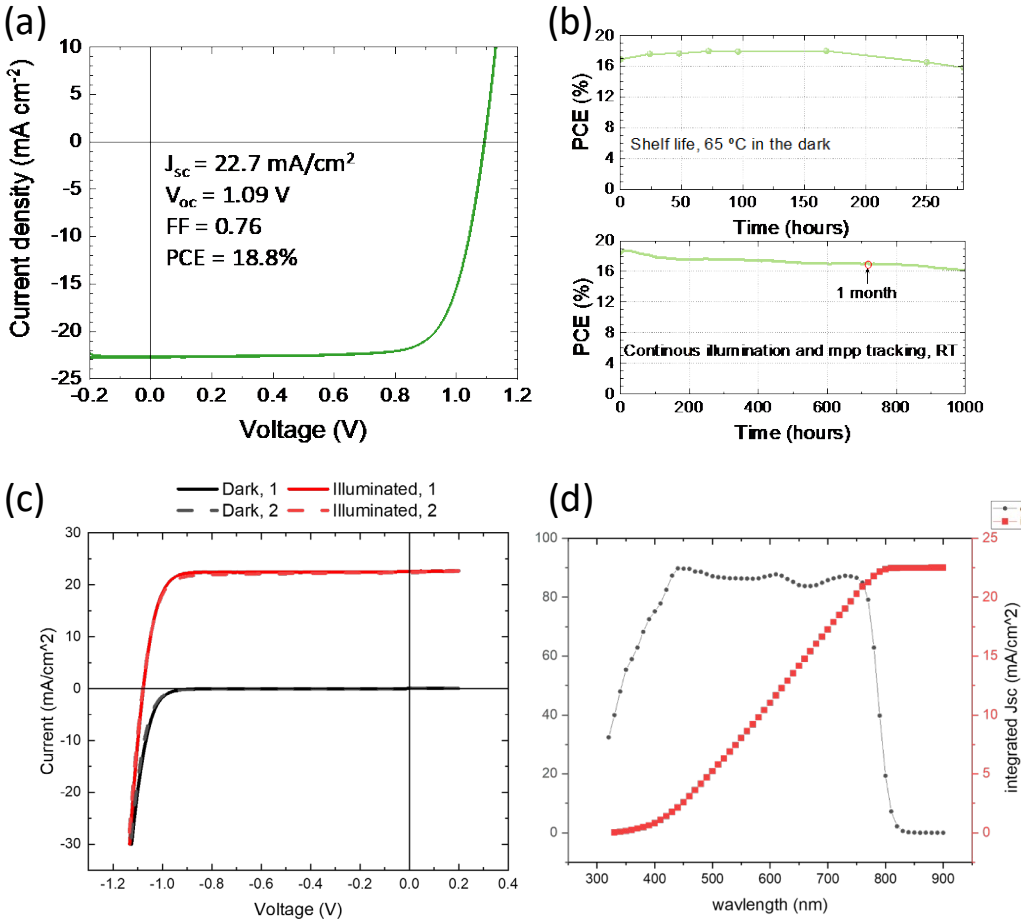

Figure 1. Examples of $FAPbI_3$ perovskite solar cells from the Valhalla consortium. (a) J-V curves and PV performance parameters for vacuum deposited $FA_yMA_{1-y}PbI_3$ solar cells with (b) preliminary stability data at high temperature (top) and under illumination (bottom). (c) Thermally evaporated $CsFAPbI_3$ perovskite solar cell (c) J-V curve and solar cell performance parameters measured under AM1.5 100 mW cm² irradiance. (d) External Quantum Efficiency Spectra giving a PV band gap of 1.56 eV.

- **Low bandgap perovskites, i.e. Eg < 1.4**. This represents the optimal bandgap to achieve the highest power conversion efficiency under solar illumination. The materials in this spectral range are based on a mixture of Sn-Pb as metal cation. Importantly, it is a system which has been poorly investigated and optimized so far when processed through vapour deposition, thus it will deserve further check in the next in the next 12 months. Based on the information collected so far we have selected the $Cs_yFA_{1-y}SnPbI_3$ (where y ~ 0.2) This composition showed good light/room temperature stability. Notably the aging under temperature was showing a second-stage crystallization process, inferred by the increase in light absorption strength near the band edge over aging time, which tells us that there is room for further improvement of the pristine films processing (see Figure 2).

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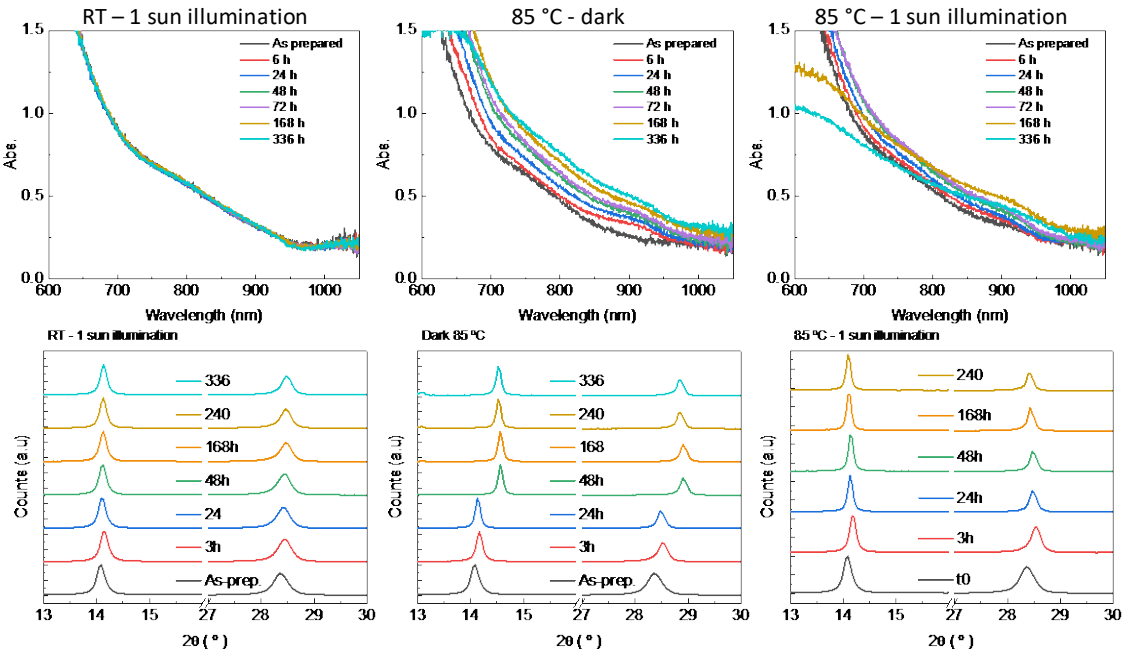

Figure 2. Absorpion spectra (top) and corresponding diffraction patterns (bottom) for vacuum deposited, low bandgap, $CsFASnPbI_3$ films measured over time and under different stress conditions (RT and illumination, 85 °C in the dark, and 85 °C under illumination).

- **Wide bandgap perovskites i.e. Eg >1.8.** This spectral range represents the optical bandgap to meet the requirements dictated for the optimization of photovoltaic devices for indoor applications, in regard of the Objective 2.3. Here the composition $Cs_yFA_{1-y}Pb(I_xBr_{1-x})_3$ has been selected. There is not yet am internationally accepted standard for characterizing solar cells for indoor applications, but a general consensus that the irradiance is typically white light LEDs and hence has no IR components. Thus optimum band gaps for absorbers for indoor use lye in the 1.8 to 2eV range. We have chosen a composition towards the wider band gap range, and specifically, initial tests have been performed on a composition which provides a bandgap of 1.94 eV with 66%Br and 25%Cs. Importantly, this composition, not only respect the spectral requirements, but also and allows the fabrication of a solar cell with a Voc of 1.37 eV (Figure 3). This works is progressing well in the direction of achieving perovskite PV cells with >1.7eV bandgap delivering over 1.4V Voc under indoor lighting conditions (Objective 2.4).

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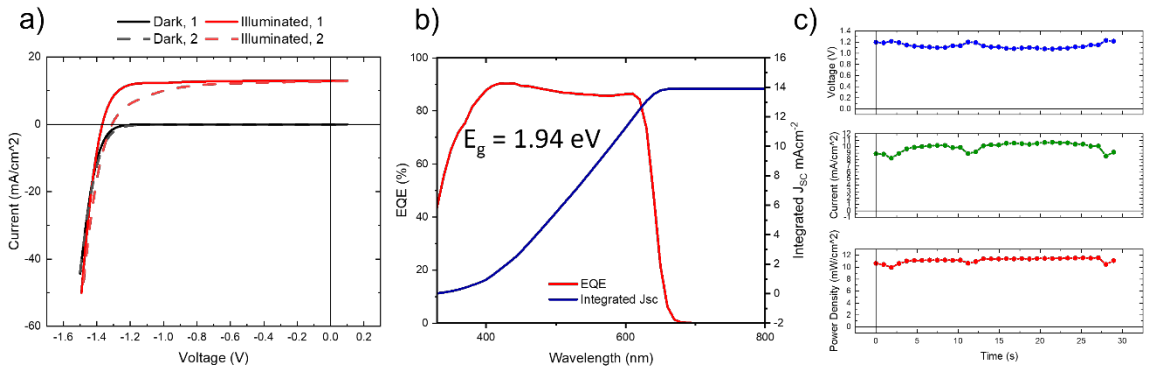

Figure 3. a) current-voltage characteristic of a solar cell fabricated with $Cs_{25}FA_{75}PbI_{34}Br_{66}$ perovskite thin film, showing an open circuit voltage of 1.37 V. b) The device External Quantum Efficiency (EQE), showing a bandgap of 1.94 eV. C) The figure of merit of the device tested at maximum power point.

1.2. Relation with other activities in the project

The activity and output of this deliverable is strictly correlated with the activity and the objectives of the WP2. We have demonstrated some device performance here by integrating the absorbers into standard solar cell device stacks, as a means of illustrating the utility of the solar absorber materials. However, these films must be further validated and optimised when the thin films are interfaced with the charge extraction layers, as developed in WP1, and the whole device stack, as needed in WP2.

2. Conclusions

In conclusions, we have identified initial perovskite absorber compositions for each spectral interval of interest based on the final aim of obtaining efficient and stable single junction devices. In the middle band gap range (1.5 < Eg < 1,7) , $FAPbI_3$, $Cs_yFA_{1-y}Pb(I_xCl_{1-x})_3$ or $FA_yMA_{1-y}PbI_3$ compounds will be further investigated. The main target will be the phase stabilization while keeping high PCE value in view of the achievement of O2.1. In the low bandgap range (Eg < 14 eV), $Cs_yFA_{1-y}Pb\ SnI_3$ compound has been chosen, this can in principle provide the ideal bandgap for the highest PCE device, however, this is very preliminary work performed both within the network and in literature about this system process through vapour deposition. Therefore, more effort will be focused on the processing optimization. In the wide bandgap range, the main directions have been provided by the target of achieving a semi-transparent solar cell and a device capable of delivering an open circuit voltage > 1.4 eV for indoor light harvesting applications. Based on this the $Cs_yFA_{1-y}Pb(I_xCl_{1-x})_3$ with with 66%Br and 25%Cs nominal content has been chosen.

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