

IMPERIAL

Formation Pathways and Phase Behaviour of CsPbI_2Br : Toward Stable and Reproducible Solar Cells

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*To you who gave support without constraints,
who loved without conditions,
who sacrificed without expectation.*

To you, Mama and Baba.

Abstract

Despite the progress in Cs-based perovskites, fabricating reproducible, phase-pure Cs-based perovskites, specifically CsPbI₂Br films under ambient conditions remains challenging. Existing methods rely on glovebox processing and antisolvents, limiting scalability. There is a need to understand how hold time, temperature, and cooling rates govern crystallisation pathways, void formation, film energetics, and device performance. In this thesis, we introduce the concepts of pre-annealing hold-time and temperature (Ch. 4) and warm-air-assisted, slow-cooling processing (Ch. 5), which aim to improve reproducibility and ambient-air stability. In the pre-annealing hold-time and temperature study, we systematically controlled pre-annealing hold times (0-40 minutes) and temperatures (RT and 10-20 °C). Through in-situ XRD and FTIR, we clarify the role of the pre-annealing hold time, and through combined SEM, void distribution analysis, and solar cell performance evaluation, we conclude that a hold step at 15 °C yields the highest performance and reproducibility. In the warm-air-assisted, slow-cooling processing project, we employed 50 °C warm air during spin-coating to achieve air-stable films. We also investigated the impact of the annealing time and cooling rate on the final film quality. We distinguished between the impact of p-type doping through the incorporation of oxygen and the effect of relieving strain through slow-cooling on the photoluminescence of the film and hence on the solar-cell performance.

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“And the last of their call will be, ‘Praise to Allah, Lord of the worlds!’
— Surah Yunus (10:10)

List of Publications

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List of Abbreviations

Abbreviation	Meaning
AFM	Atomic Force Microscopy
AM 1.5G	Air Mass 1.5 Global (standard solar spectrum)
APV	Asymmetric Pseudo-Voigt (peak model)
APS	Atmospheric Pressure Photoelectron Spectroscopy
APXPS	Ambient Pressure X-ray Photoelectron Spectroscopy
ARXPS	Angle-Resolved X-ray Photoelectron Spectroscopy
ATR-FTIR	Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy
BCP	Bathocuproine
BSE	Backscattered Electrons (in SEM)
CB	Conduction Band
CBM	Conduction Band Minimum
CsPbI ₂ Br	Caesium Lead Iodide–Bromide (perovskite)
DMF	N,N-Dimethylformamide
DMSO	Dimethyl Sulfoxide
DOS	Density of States
DSSC	Dye-Sensitised Solar Cell
E_f	Fermi level
E_g	Bandgap (energy difference between CBM and VBM)
E_{vac}	Vacuum energy level
EIS	Electrochemical Impedance Spectroscopy
EQE	External Quantum Efficiency
ETL	Electron Transport Layer
FF	Fill Factor
FTIR	Fourier Transform Infrared Spectroscopy
FTO	Fluorine-doped Tin Oxide
GIXRD	Grazing-Incidence X-ray Diffraction
HOMO	Highest Occupied Molecular Orbital
HTL	Hole Transport Layer
IE	Ionisation Energy
ITO	Indium Tin Oxide
J_{ph}	Light-generated photocurrent
J_{sc}	Short-Circuit Current Density

J–V	Current Density–Voltage
KP	Kelvin Probe
LED	Light-Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
MAPbI ₃	Methylammonium Lead Iodide
MeO-2PACz	[2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid
MPP	Maximum Power Point
ND	Neutral Density (filters)
PCE	Power Conversion Efficiency
PCBM/C ₆₀	Phenyl-C ₆₁ -butyric acid methyl ester / Fullerene (C ₆₀)
PL	Photoluminescence
PSC	Perovskite Solar Cell
PV	Photovoltaic
R _s	Series Resistance
R _{sh}	Shunt Resistance
RT	Room Temperature
SC	Spin-Coating
SCR	Space-Charge Region (depletion region)
SE	Secondary Electrons (in SEM)
SEM	Scanning Electron Microscopy
SnO ₂	Tin Dioxide (electron transport/interlayer)
SRH	Shockley–Read–Hall (recombination)
TCSPC	Time-Related Single Photon Counting
TEC	Thermal Expansion Coefficient
TRPL	Time-Resolved Photoluminescence
UV-Vis	Ultraviolet–Visible Spectroscopy
VB	Valence Band
VBM	Valence Band Maximum
V _{oc}	Open-Circuit Voltage
WF (Φ)	Work Function
Φ _B	Schottky barrier height
Φ _m	Metal work function
Φ _s	Semiconductor work function
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

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Chapter 1: Introduction

The continuous increase in global population and industrial growth puts high demand on renewable and environmentally friendly energy sources. Clean energy is energy that is generated with little to no greenhouse gas emissions or other harmful pollutants during operation. Yet, as of 2024, clean energy contributed only about 40% of global electricity generation ¹. This includes contributions from solar, wind, hydro, and nuclear energy, with solar showing the fastest growth rate among them. While this is a good improvement, there is still a need for further enhancement, which inspired many national initiatives. For instance, the UK is committed to achieving 95% low-carbon electricity ², and Saudi Arabia is targeting 50% renewable energy generation by 2030, as well as a net-zero carbon emissions by 2060 ³. These goals align with other international targets and reflect a wider drive toward diversified and sustainable energy systems. Sunlight is one of the most abundant natural resources, reaching the Earth in quantities exceeding daily human energy needs. This makes solar energy an extremely attractive source of clean energy. It is estimated that the sun delivers around 173,000 terawatts of continuous solar power to Earth, more than 10,000 times the world's current total energy use ^{4,5}.

Silicon-based solar cells were first commercialised in 1954 with a power conversion efficiency (PCE) of just 4.5%, which has since become the dominant photovoltaic (PV) technology ⁶. They now account for over 90% of the global PV market and are widely used on residential and commercial scale applications⁷. Current in lab-scale monocrystalline silicon cells exceeds 27% PCE ⁸. These achievements were driven by the aim to reduce the electricity generation costs, which reached \$0.038 to \$0.078 per kWh ⁹. This price range places solar energy among the most cost-competitive sources of electricity globally. However, despite these remarkable advances, single-junction silicon solar cells are fundamentally constrained by the Shockley–Queisser⁶ limit, which restricts the maximum theoretical efficiency of a single absorber to ~33% under standard illumination. This limitation arises because photons with energies below the silicon bandgap are not absorbed, while photons with energies well above the bandgap lose excess energy as heat through thermalisation. As silicon technology approaches this fundamental efficiency ceiling, further performance gains can no longer be achieved through improvements in material quality or device engineering alone. Instead, overcoming this limit requires tandem architectures, where two absorbers with complementary bandgaps are stacked to utilise a broader portion of the solar spectrum. In this context, metal-halide perovskites have emerged as uniquely attractive top-cell materials for silicon tandem photovoltaics. Their tunable bandgap, high absorption coefficient, solution processability, and compatibility with low-temperature fabrication enable them to be integrated directly onto existing silicon technologies. Rather than replacing silicon, perovskites offer a pathway to extend the performance of the

established PV platform beyond its single-junction limits, with demonstrated tandem efficiencies already exceeding 33%.⁷

1.1 Historical Development of Perovskite Solar Cells (PSCs)

The first perovskite solar cell (PSC) was reported by Kojima et al. in 2009, where methyl ammonium lead iodide (MAPbI_3), a metal halide perovskite was used as the photosensitiser in a dye-sensitised solar cell (DSSC), achieving a PCE 3.8%¹⁰. Despite this relatively modest performance, this study marked a breakthrough, demonstrating the potential of PSCs and initiating further research in the field. In 2011, Park et al. further improved the solar cell structure by optimising the mesoporous TiO_2 thickness and depositing perovskite quantum dots on the surface of the TiO_2 , achieving a 6.5% PCE¹¹. A year later Kim et al. developed a new device architecture now known as the thin-film solar cell structure by replacing the liquid electrolyte with 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD), which also enhances perovskite stability, achieving an impressive 9.7% PCE¹². In the following months, Lee and Snaith reported using Al_2O_3 mesoporous structure atop of a compact TiO_2 layer. The perovskite was then deposited to cover the surface of an Al_2O_3 mesoporous structure, increasing the open-circuit voltage (V_{oc}) and pushing PCE to 10.9%¹³. In 2012, Etgar et al. reported the first fully planar perovskite solar cell, demonstrating MAPbI_3 as both absorber and hole-transport layer in a simple $\text{TiO}_2/\text{MAPbI}_3/\text{Au}$ junction, marking a clear shift away from DSSC-type operation. In 2013, Jeng et al. introduced the first p-i-n perovskite solar cell using a PEDOT:PSS/ MAPbI_3 /PCBM architecture, establishing the inverted configuration used in many subsequent PSC designs. Later in 2013, the next PCE record, 15%, was achieved by Burschka et al., who reported two-step deposition of the perovskite active layer, whereby a film of PbI_2 was first deposited, followed by the deposition of a solution of MAI. This resulted in a compact MAPbI_3 film that fully infiltrated the entire mesoporous TiO_2 structure¹⁴.¹⁵ In the following studies, the PCE of planar devices reached and eventually surpassed those of mesoporous architecture PSC 16–18.

The continued development of PSCs was achieved through a broad spectrum of studies that focused on crystallisation control, stability, and scalability. One of the significant breakthroughs in the field was reported in 2014 by Jeon, who worked on crystallisation control. This was achieved by introducing dimethyl sulfoxide (DMSO) to form PbI_2 -DMSO adducts to control the formation of the intermediate phase, as well as developing the antisolvent deposition method, where toluene is dripped on the perovskite during the spin coating process. This made a significant improvement in the quality of the perovskite film process, resulting in a very compact and uniform film, which led to a 16.2% PCE¹⁹. This work inspired many studies that further develop the anti-solvent deposition technique^{20–26}. In 2015, the same group

investigated mixed formadinium (FA) and MA cation perovskites to improve the stability of the FAPbI_3 structure. The rationale was to improve the Goldschmidt tolerance factor (GTF) through balancing the large FA size with MA (reducing the average A-site ionic radius). Mixed cations and mixed melas have been further optimised in the following studies to improve phase stability and tune bandgap^{27–32}. In recent years, the field has also been heading towards investigating Pb-Sn Perovskites. Besides having better phase stability, this research shift toward Pb-Sn was inspired by their narrow bandgap which makes them suitable as bottom sub-cell for all-perovskite tandem solar cells, suppressed Sn oxidation via Pb substitution, and balanced carrier dynamics which is achieved by the passivation effect of Pb^{2+} and high mobility of Sn^{2+} ³³. To date, the highest reported single-junction PSC PCE is 26.7%³⁴.

In addition to improving stability, incorporating large cations into the perovskite structure also enabled the development of 2D/3D perovskite, which improves moisture stability, thermal stability, and acts as a 3D perovskite passivator^{35–40}. To push the technology towards commercialisation, the research community started addressing the challenges of scalability. In 2017, researchers at École Polytechnique Fédérale de Lausanne (EPFL) reported fabricating large area ($\sim 100\text{ cm}^2$) 2D/3D hybrid perovskite modules that maintained a PCE $< 11.2\%$ over 10,000 hours of continuous operation. This breakthrough was one of the first steps taken to move the technology closer towards commercialisation, record was later pushed to a PCE of 23.3%^{41,42}. With compositional and crystallisation strategies established, further advances in PSC research between 2018 and 2023 turned toward tandem integration, encapsulation, and mechanical robustness. At the time of writing the highest reported perovskite/silicon tandem solar cell PCE is 34.6%³⁴.

1.2 Development of Inorganic Cs-Pb Perovskite Solar Cells

Alongside the developments of organic-inorganic PSC during the 2010s, the development of all-inorganic PSC (IPSC) started. Cs-based perovskites offer superior thermal stability and resistance to phase segregation compared with their MA- and FA counterparts. Kulbak *et al.* reported that Cs-based compounds decompose at significantly higher temperatures than their organic counterparts, confirming their enhanced thermal resilience⁴³. The first report of an IPSC was in 2012, in a study demonstrating a CsSnI_3 device with an ITO/ CsSnI_3 /Au/Ti architecture. This work initiated the transition from hybrid to fully inorganic perovskites⁴⁴. However, Sn-based perovskites suffered from severe oxidation of Sn^{2+} to Sn^{4+} , leading to poor stability and low efficiency⁴⁵. The first reported lead-based IPSC was in 2014 by Kim *et al.*, who substituted MA with Cs in MAPbI_3 to form CsPbI_3 . The resulting device achieved a PCE of just 0.09%, primarily due to the instability of CsPbI_3 in its photoactive phase at room temperature³⁰. This solar cell still struggled with phase instability due to the poor tolerance

factor of Cs-based perovskites due to the significantly small size of Cs atoms ^{27,30,46,47}. In a key study, Snaith *et al.* modified the synthesis process by introducing hydroiodic acid (HI) into the precursor solution. This approach altered the crystallisation dynamics, yielding films with improved uniformity and suppressing the formation of photo-inactive phases at reduced annealing temperature (from 335 °C to 100 °C). These improvements enabled the fabrication of devices with a PCE of 2.9 % and significantly enhanced the ambient stability of the α -phase ⁴⁷. Following studies suggested that the stabilising effect of HI in CsPbI₃ films may stem from dimethylammonium (DMA) incorporation, which is a byproduct of HI-DMF interaction, rather than HI alone. However, it was then confirmed that due to the volatility nature of DMA, it is not incorporated in the final crystal structure and that HI does not lower the formation temperature of the photoactive phase but rather improves bromide solubility ^{48–50}.

The following advances focused on improving device performance and stability through doping and passivation strategies. Han *et al.* used CaCl₂ as an additive to achieve n-type doping in CsPbI₂Br, which enhanced crystallinity, suppressed trap states, and improved the built-in potential. Their optimised device achieved a record PCE of 16.79 % and maintained 90% of its initial efficiency after 1000 hours in air ⁵¹. Ozturk *et al.* have also demonstrated that FeCl₂ doping in CsPbI₂Br can stabilise the black α -phases (phases of Cs-Based perovskites are fully explained in the next chapter), improve crystallinity, and enhance energy-level alignment. Their device achieved a record PCE of 17.1 % with over 95% efficiency retention after 330 hours of continuous operation ⁵².

To address phase instability, Wang *et al.* employed phenylethylammonium (PEA⁺) cations for surface termination, which helped form a defect-passivated surface and stabilised CsPbI₃ against moisture. The corresponding PSCs exhibited stabilised efficiencies of 13.5 % ⁵³. The mixed-halide perovskite CsPbI₂Br became another focal point due to its enhanced phase stability and moderate bandgap (~1.92 eV). Chen *et al.* achieved a PCE of 16.07 % using a gradient thermal annealing (GTA) and anti-solvent (ATS) process to produce high-quality, uniform films with low defect density ⁵⁴. Ma *et al.* extended this approach by applying a secondary crystallisation step with guanidinium bromide. This further improved crystallinity, passivated defects, and tuned the Fermi level, resulting in 16.97% PCE and high operational stability ⁵⁵. The highest Cs-Pb based solar cell PCE reported in 2023, which is 18.49% ⁵⁶.

1.3 Aims of this work

Despite recent advances, inorganic CsPb-based PSCs still suffer from performance limitations. Reproducibility of film formation remains a persistent challenge, mainly due to the sensitivity of film formation to subtle variations in fabrication conditions. Buried voids and

incomplete coverage at the perovskite-charge transport interfaces frequently lead to poor charge extraction and increased non-radiative recombination losses. The fabrication process is highly sensitive to the fabrication environment, making it difficult to maintain consistency outside of controlled settings. Furthermore, achieving long-term phase stability of the photoactive α -phase under ambient air remains a significant obstacle. In particular, exposure to moisture and oxygen continues to degrade device performance over time. Although several studies have explored air-processing methods to improve ambient stability, these approaches typically rely on annealing in dry air or require elevated air temperatures during spin coating, which introduces additional complexity.

This thesis aims to address these challenges by developing scalable, antisolvent-free fabrication strategies that improve both the reproducibility and the long-term stability of CsPbI₂Br-based devices under ambient processing conditions. Two complementary approaches are introduced and systematically investigated.

First, we explore the effect of pre-annealing hold time and temperature on film formation dynamics. By introducing a controlled hold step prior to thermal annealing, we demonstrate that intermediate-phase formation can be steered towards more uniform crystallisation, resulting in improved film coverage and reduced buried interface voids. The influence of hold time (0-40 min) and temperature (RT and 10-20 °C) is systematically studied using a combination of *in-situ* structural, optical, and morphological characterisation techniques. This enables us to establish a clear correlation between processing parameters, void formation, and device performance, ultimately identifying an optimal hold condition that maximises reproducibility and efficiency.

Second, we present a warm-air-assisted, slow-cooling processing strategy designed to stabilise the α -phase and enhance photoluminescence intensity under ambient air. This gentle 50 °C processing approach allows controlled oxygen incorporation and gradual strain relaxation, leading to phase-pure, pinhole-free films with significantly enhanced emission intensity and improved air stability. The effects of annealing duration and cooling rate are deconvoluted to distinguish between the roles of oxygen-driven surface doping and lattice-strain relief in suppressing non-radiative recombination.

Together, these approaches provide a practical and mechanistically informed framework for improving film quality, device reproducibility, and operational stability, offering valuable insights into the scalable fabrication of high-efficiency all-inorganic perovskite photovoltaics.

Chapter 2: Theoretical Background

2.1 Atoms Interaction and Molecule Formation

As two atoms approach each other, a covalent bond starts to form through the overlap of the orbitals of these atoms, resulting in a new set of molecular orbitals. To fully understand this interaction, let us consider the simplest case of two hydrogen atoms, each possessing one 1s atomic orbital. As the distance between the two atoms reduces, the attraction between the positively charged nucleus and the negatively charged electrons reduces the total potential energy of the system. This is illustrated in Figure 1a, where the total energy curve exhibits a minimum at a specific intermolecular distance, denoted by x . This minimum represents the most energetically favourable configuration, known as the bonding state. As the atoms continue to approach each other beyond the threshold, x , repulsive interactions become dominant, resulting in a rapid increase in total energy that exceeds the energy of the two isolated atoms. The repulsion is primarily due to the Coulomb repulsion between nuclei. This resulting state is referred to as the antibonding state. Figure 1(b) illustrates the interatomic force as a function of distance, showing that the bonding state corresponds to a point of maximum attractive force. In contrast, the antibonding state is at a high repulsive force. Similarly, the molecular units in organic materials are typically held together not by shared electron pairs but through van der Waals forces, which are relatively weak, non-covalent interactions arising from transient dipoles ⁵⁷.

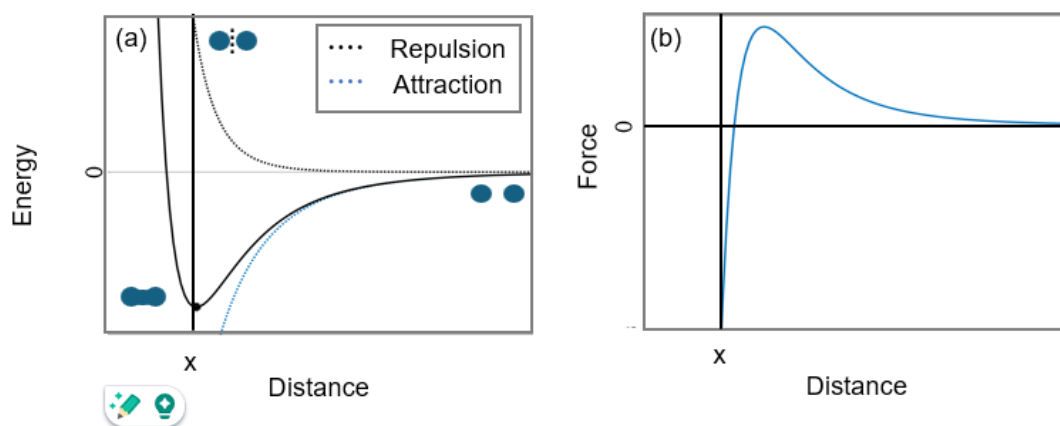


Figure 1- (a) Potential energy and (b) force between two atoms as a function of distance, showing equilibrium at x where attraction and repulsion balance. ⁵⁷

2.2 Band Structure and Electronic Energy Levels

2.2.1 Bandgap Fundamentals

In solid-state physics, band theory describes how atomic orbitals from individual atoms combine in a crystalline solid to form extended states called energy bands. When atoms are arranged periodically

in a crystal lattice, their discrete energy levels expand into continuous bands. As illustrated in Figure 2, the more atoms are added, the more the number of available molecular orbitals increases, and the energy differences between them diminish, resulting in two principal bands: the valence band (VB) and the conduction band (CB). The VB is primarily composed of bonding states, while the CB consists of antibonding states. These bands are separated by a region of forbidden energy known as the bandgap (E_g), where no electronic states are permitted⁵⁷.

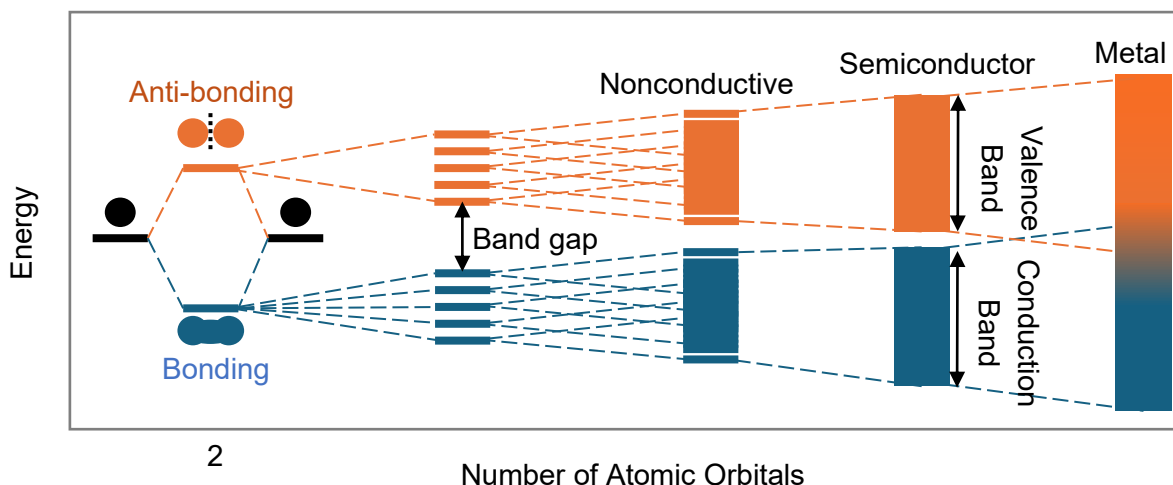


Figure 2- Evolution of energy levels with increasing atomic orbital overlap. As more atoms interact, discrete bonding and antibonding molecular orbitals form energy bands. The bonding orbitals (blue) broaden into the VB, while the antibonding orbitals (orange) form the CB. The energy separation between these bands corresponds to the bandgap of the material⁵⁷.

At absolute 0 K, electrons populate the VB completely, leaving the CB empty. The highest energy level occupied in the VB is termed the VB maximum (VBM), which corresponds to the highest occupied molecular orbital (HOMO) in organic semiconductors. Conversely, the CB minimum (CBM) marks the onset of available states in the CB, analogous to the lowest unoccupied molecular orbital (LUMO) in molecular systems. The E_g is defined as the energy difference between CBM and VBM, which determines a material's ability to conduct electricity and absorb photons. Materials are broadly classified based on the magnitude of their bandgap: Insulators ($E_g > 3$ eV), Semiconductors ($0 < E_g < 3$ eV), and Metals ($E_g \approx 0$ eV.)

Electrons can transition from the VB to the CB if provided with sufficient energy, typically via thermal agitation or photon absorption. This process leaves behind holes in the VB, enabling charge transport. The free electron and hole densities are denoted as n and p , respectively.

The density of states (DOS), $g(E)$, is the number of available electronic states at a given energy per unit volume. It is a fundamental parameter that governs carrier statistics and optical absorption. The DOS in the CB and VB can be approximated by:

$$g_c(E) = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_c} \quad \text{For } E > E_c \quad \text{Equation 1}$$

$$g_v(E) = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} \sqrt{E_v - E} \quad \text{For } E < E_v \quad \text{Equation 2}$$

where m_e^* and m_h^* are the effective masses of electrons and holes, respectively. $\hbar$ is Planck's constant, and E_c and E_v are the CB and VB energies, respectively.

2.2.2 The Fermi Level and Electronic Distribution

The Fermi level (E_f) is a theoretical reference point representing the energy at which the probability of occupation by an electron is exactly 50%. The Fermi-Dirac function describes this statistical distribution:

$$f(E) = \frac{1}{1 + e^{\frac{E - E_f}{kT}}} \quad \text{Equation 3}$$

Where E is energy, k is the Boltzmann constant, and T is temperature. At 0 K, all states below E_f are fully occupied, while those above are empty. At finite temperatures, the function takes an S-shaped curve, indicating a gradual transition in occupancy.

In intrinsic undoped semiconductors, E_f lies at the middle of the E_g , reflecting equal concentrations of electrons and holes. By introducing impurities (a process called doping) E_f can be manipulated:

- n-type doping introduces atoms with more valence electrons than the host atoms (e.g., phosphorus in silicon), supplying extra electrons and shifting E_f closer to the CB.
- p-type doping introduces atoms with fewer valence electrons (e.g., boron in silicon), creating holes and moving E_f toward the VB.

The change in E_f due to doping is quantified as:

$$E_f = E_i + kT \ln \left(\frac{n}{n_i} \right) \text{ for n-type semiconductor} \quad \text{Equation 4}$$

$$E_f = E_i - kT \ln \left(\frac{p}{n_i} \right) \text{ for p-type semiconductor}$$

Where, n_i is the intrinsic carrier concentration. When doping levels are high, $n \approx N_D$ for n-type and $p \approx N_A$ for p-type semiconductors, where N_D and N_A are the donor and acceptor concentrations, respectively.

Figure 3 shows the flat band structures and E_f for three cases: (a) intrinsic, (b) n-type, and (c) p-type

semiconductors, along with the corresponding Fermi-Dirac distribution function $f(E, T)$. In the intrinsic case (a), the E_f is positioned near the middle of the bandgap. For the n-type material (b), the E_f shifts closer to the CB, whereas in the p-type material (c), it moves toward the VB. The function $f(E)$ appears as a step function at 0 K and gradually takes on an S-shaped curve at higher temperatures ⁵⁷.

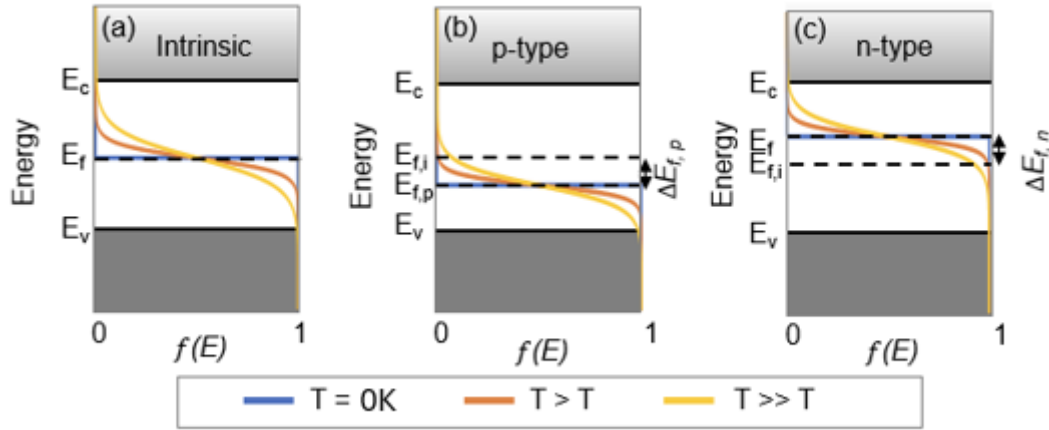


Figure 3 - The flat band structures and Fermi levels for three cases: (a) intrinsic, (b) n-type, and (c) p-type semiconductors, along with the corresponding Fermi-Dirac distribution function $f(E, T)$ ⁵⁷

2.2.3 Vacuum Level, Work Function, and Interfacial Alignment

The vacuum energy level (E_{vac}) is the energy of a free electron at rest just outside a material. All energy levels within a material are measured relative to this vacuum level. Therefore, the position of the E_f with respect to E_{vac} becomes particularly important and is referred to as the work function (Φ). Φ is defined as the minimum energy required to remove an electron from the E_f to the v ($\Phi = E_{vac} - E_f$).

The ionisation energy (IE) is the energy needed to remove an electron from the VB Maximum to the E_{vac} . On the other hand, the energy released when an electron is added from E_{vac} to the CB minimum is referred to as Electron affinity (χ).

All three quantities (Φ , IE, and χ) are central in understanding energy level alignment at interfaces between different materials. For instance, in organic and perovskite photovoltaics, proper alignment of these levels ensures efficient charge extraction and minimal energy loss. These concepts are illustrated in Figure 4 and further elaborated through interfacial diagrams and experimental measurements in surface science.

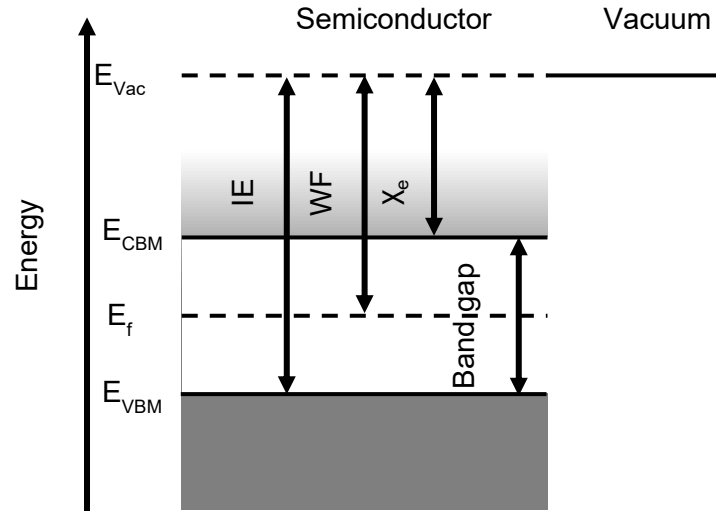


Figure 4 - Flat band diagram of a semiconductor in vacuum, highlighting the key energy levels relative to the vacuum level. ⁵⁷

2.3 Semiconductor devices fundamentals

2.3.1 p-n Junction

When a p-type (excess holes) and an n-type (excess electrons) semiconductor are brought into contact to form a p-n junction, their band structures must realign to reach thermal equilibrium. Before contact, the only common energy reference between the two materials is the E_{vac} . While the E_g of each material may differ in general, idealised models often assume identical E_g for simplicity ⁵⁷. Each isolated material has its own E_f . The difference in E_f creates a concentration gradient that drives carrier diffusion once the junction is formed.

As shown in Figure 5 a, upon contact between the n-type and p-type regions, charge carriers begin to diffuse due to the concentration gradient: electrons, which are the majority carriers in the n-type region, diffuse into the p-type side, while holes, the majority carriers in the p-type region, diffuse into the n-type side. As electrons leave the n-type region, they expose positively charged donor ions that are no longer neutralised by mobile electrons. Similarly, as holes leave the p-type region, negatively charged acceptor ions are left behind. These exposed ionic charges are immobile, being fixed in the crystal lattice, and they accumulate near the junction interface. The result is the formation of a region on both sides of the junction where mobile charge carriers are depleted known as the depletion region.

This region is electrically active despite being free of mobile carriers. The spatial separation of fixed positive and negative charges generates an internal electric field that points from the n-type side toward the p-type side. This field establishes a built-in potential and creates an electrostatic force that opposes further diffusion of carriers. As a result, the system moves toward electrostatic equilibrium, where drift and diffusion forces are balanced, and no net current flows under zero external bias. As

this charge redistribution progresses, the energy bands bend to reflect the new electrostatic environment. The CB and VB on the n-type side bend downward, and those on the p-type side bend upward. This continues until the system reaches equilibrium, at which point the E_f becomes constant throughout the entire junction. The electric field created by this charge separation establishes a built-in potential Φ_{bi} , which represents the energy barrier that must be overcome for majority carriers to cross the junction. It is defined by the difference in work functions between the p-type and n-type regions ($\Phi_{bi} = \Phi_p - \Phi_n$).

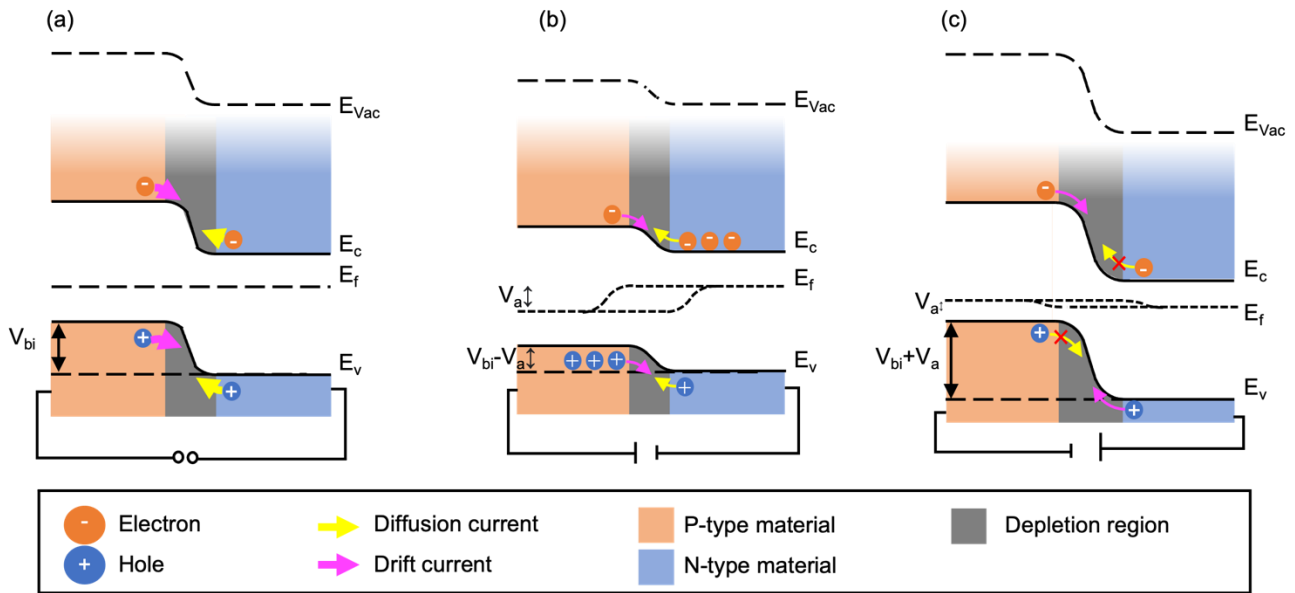


Figure 5 - Schematic illustrations of a p-n junction at (a) equilibrium under (b) forward and (c) reverse bias. ⁵⁷

Forward bias of a p-n Junction

As illustrated in Figure 5 b, under forward bias, the p-type side of the p-n junction is connected to a higher electrical potential relative to the n-type side. This external bias opposes the built-in electric field established at equilibrium and reduces the built-in potential barrier Φ_{bi} that normally resists the motion of majority carriers. As a result, the energy bands in the p-type region shift downward. In contrast, the bands in the n-type region shift upward, effectively lowering the energy difference between the CB edge of the n-type region and the VB edge of the p-type region. This modification to the band profile decreases the width of the depletion region, facilitating carrier transport across the junction.

With the potential barrier lowered, majority carriers on both sides can more readily diffuse into the opposite regions. Electrons in the n-type CB, where their concentration is highest, diffuse toward the p-type side, driven by the concentration gradient. Once they cross the junction, they enter the p-type region and recombine with holes in the VB. Similarly, holes in the p-type VB diffuse toward the n-type

side and recombine with electrons in the CB. These diffusion processes constitute the dominant current flow under forward bias, as the population of majority carriers is significantly higher than that of minority carriers in each region.

While majority carriers move primarily by diffusion, minority carriers also experience motion due to drift. In the p-type region, a small population of thermally generated electrons exists in the CB. These electrons, being minority carriers, are influenced by the residual electric field in the depletion region and drift toward the n-type side. In parallel, minority holes present in the n-type VB are swept across the junction toward the p-type side under the influence of the same electric field. Although these minority carrier drift currents flow in the opposite direction to the majority carrier diffusion currents, they are much smaller in magnitude and do not contribute significantly to the total current under forward bias.

Overall, the reduction in the potential barrier and narrowing of the depletion region allow for a substantial increase in the injection of majority carriers across the junction. The resulting net current increases exponentially with the applied forward voltage and is described by the Shockley diode equation:

$$I = I_0(e^{\frac{qV}{kT}} - 1) \quad \text{Equation 5}$$

Reverse Bias of a p-n Junction

On the other hand, and as illustrated Figure 5 c, when a p-n junction is placed under reverse bias, the p-type side is connected to a lower electrical potential than the n-type side. This external voltage adds to the built-in potential of the junction, effectively increasing the total potential barrier that charge carriers must overcome to move across the depletion region. In energy terms, the conduction and VBs bend more steeply, and the depletion region widens. This widening occurs because the externally applied electric field reinforces the built-in field, sweeping mobile majority carriers away from the junction and further depleting the area near the interface of free charge carriers.

As a result, the movement of majority carriers (electrons in the n-type and holes in the p-type) is strongly suppressed, and diffusion current is effectively eliminated. In this state, the current due to majority carrier flow becomes negligible, and under ideal conditions, no current would flow at all. However, in real semiconductors, a small but finite current persists under reverse bias. This current arises due to the presence of minority carriers on each side of the junction. In the p-type region, a small population of thermally generated electrons exists, and in the n-type region, thermally generated holes are present. These minority carriers are continuously generated by thermal excitation and are swept across the junction by the strong electric field in the depletion region. Because they are driven by the field rather than a concentration gradient, their motion constitutes a drift current.

This minority carrier drift current is known as the leakage current or reverse saturation current (I_0). Its magnitude is determined by the rate of thermal generation of carriers and is typically very small, on the order of nanoamperes or less in high-quality silicon diodes. This current flows in the direction opposite to that of forward-bias diffusion current, from the p-type to the n-type side. The reverse saturation current is mainly independent of the applied reverse voltage. It is primarily a function of temperature, material quality, and intrinsic carrier concentration. Because it involves minority carriers, even a slight increase in temperature can lead to a noticeable rise in I_0 , due to the exponential dependence of intrinsic carrier generation on temperature. Although the reverse saturation current is negligible under most operating conditions, it becomes critical in applications involving high sensitivity, low noise, or high temperatures, where leakage can impact device performance. It also sets the baseline for the total current in the Shockley diode $I = I_0(e^{\frac{qV}{kT}} - 1)$ Equation 5

Fermi Level Splitting in p-n and p-i-n Junctions

In a p-n junction, the initial difference in E_f between the p-type and n-type regions leads to carrier diffusion across the interface. Electrons flow from the n-side to the p-side, and holes flow in the opposite direction, establishing an internal electric field. This results in the formation of a depletion region, where mobile carriers are swept out. Equilibrium is reached when the E_f becomes uniform across the junction, and the built-in potential prevents further net diffusion⁵⁸. To extend the depletion region and enhance carrier separation, an intrinsic semiconductor layer can be inserted between the doped regions, forming a p-i-n junction. The intrinsic layer supports a wider electric field without contributing free carriers, improving charge extraction and reducing recombination losses⁵⁹. Under non-equilibrium conditions, such as forward bias or illumination, the E_f splits into two quasi-Fermi levels: one for electrons (E_{fn}) and one for holes (E_{fp}). The energy separation between these levels defines the internal voltage: $qV = E_{fn} - E_{fp}$. This E_f level splitting reflects the degree of carrier injection or separation and is essential in devices such as solar cells and LEDs⁶⁰.

2.3.2 Metal-Semiconductor Junctions

When metal and semiconductor brought into contact, electrons flow from the material with a higher E_f to the one with a lower E_f to equilibrate the chemical potential across the junction. The direction of this electron flow and the resulting band alignment depend on the relative WF of the metal (Φ_m) and semiconductor (Φ_s). Crucially, the depletion region forms almost entirely within the semiconductor, not in the metal. This is due to the vast difference in free carrier concentrations: metals have electron densities order of magnitude higher than that of semiconductors. Consequently, the screening length in the metal is extremely short making the band bending on the metal side negligible. In contrast, the semiconductor exhibits pronounced band bending over a relatively extended region^{58,61}.

When the metal work function exceeds that of the semiconductor (*i.e.* $\phi_M > \phi_S$), electrons flow from the semiconductor into the metal upon contact. This electron loss leaves behind positively charged ionised donor atoms in n-type semiconductors, forming a space charge region (SCR) near the interface. The resulting electric field bends the semiconductor bands upward near the junction. This barrier blocks electrons from flowing back into the semiconductor, resulting in rectifying diode-like behaviour. This is called a Schottky contact for electrons. The energy barrier created at the interface is the Schottky barrier height for an n-type semiconductor (ϕ_{Bn}): $\phi_{Bn} = \phi_M - \chi$. For p-type semiconductors, this same condition ($\Phi_m > \Phi_s$) aligns the metal E_f closer to the VB, facilitating hole injection. Thus, it can form an Ohmic contact for holes, enabling efficient current injection.

When the metal work function is lower than that of the semiconductor (*i.e.* $\phi_M < \phi_S$), electrons flow from the metal into the semiconductor, accumulating at the interface. This leads to band bending downward, and may result in electron accumulation or negligible depletion, depending on doping. The barrier height is small or non-existent, allowing majority carriers to flow easily in both directions. For p-type semiconductors, a Schottky barrier for holes may form, with the Schottky barrier height (ϕ_{Bp}) given by: $\phi_{Bp} = \phi_M - (\chi + E_g)$. For n-type semiconductors, this results in an Ohmic contact for electrons, allowing easy extraction or injection.

In summary, and as shown in Figure 5 a and b, n-type semiconductors tend to have lower work functions than typical metals, making Schottky contacts common, while p-type semiconductors generally have higher work functions, favouring Ohmic behaviour when paired with common metals. In terms of device functionality, Ohmic contacts are generally preferred for both solar cells and light-emitting diodes (LEDs), but for different reasons. For instance, in solar cells, efficient carrier extraction requires: $\Phi_m < \Phi_s$ on the n-type side to allow electrons (majority carriers) to flow into the metal, and $\Phi_m > \Phi_s$ on the p-type side to enable hole extraction into the metal. Thus, the formation of an Ohmic or Schottky contact is not solely determined by whether the semiconductor is n-type or p-type, but rather by the relative alignment between the metal's work function (Φ_m) and the semiconductor's electron affinity or ionisation energy. Careful selection of contact materials is crucial to optimise device performance in either application.

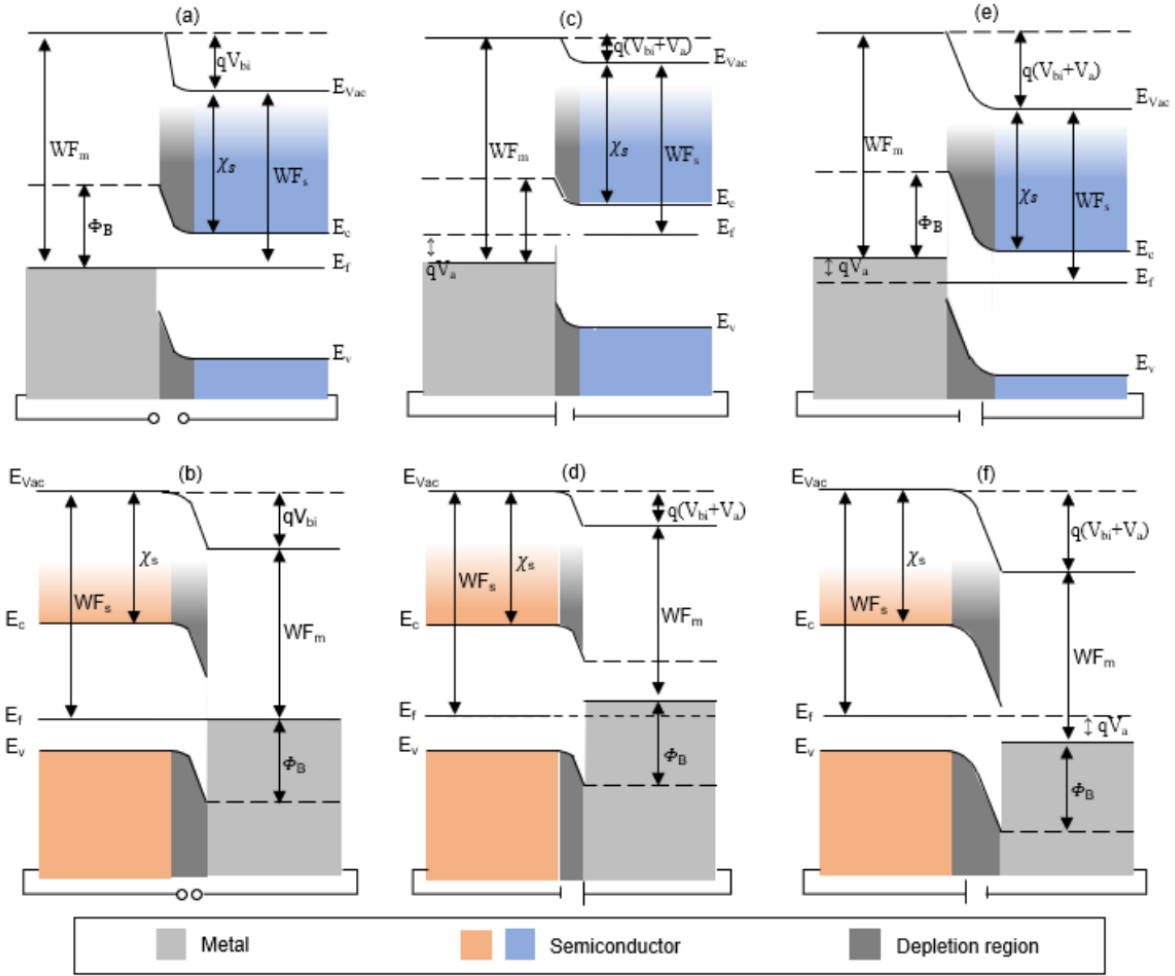


Figure 6 - The flat band structure of m-s junction where $\Phi_M > \Phi_s$ (blue) and $\Phi_M < \Phi_s$ (orange) (a) and (b) In equilibrium, a Schottky electron and an ohmic hole junction are formed. (c) and (d) Under forward bias, Φ_B and SCR decrease. (e) and (f) In reverse bias, Φ_B and SCR increase. ⁵⁷

Bias of Metal-Semiconductor Junctions

For electrons, Schottky contacts ($\Phi_m > \Phi_s$), under forward bias, the metal is connected to a higher potential, lowering $E_{f,m}$ relative to the semiconductor. Simultaneously, the semiconductor's $E_{f,s}$ shifts upward. This reduces the built-in potential (Φ_{bi}), narrows the depletion region, and decreases the energy barrier ($\Phi_B = \Phi_m - \chi$) that impedes electron flow. As a result, electron injection into the metal increases exponentially with voltage. Under reverse bias (semiconductor at higher potential) increases the $E_{f,m}$ and lowers the $E_{f,s}$. This widens the depletion region and raises the energy barrier, suppressing thermionic emission. The current becomes limited to a small reverse saturation (leakage) current due to minority carriers.

For holes Schottky contacts ($\Phi_m < \Phi_s$) under forward bias (metal more positive), $E_{f,m}$ drops and $E_{f,s}$ rises, reducing band bending and narrowing the depletion region. The barrier to hole injection decreases, enabling forward current flow. Under reverse bias increases the barrier for hole flow.

$E_{f,m}$ rises, $E_{f,s}$ falls, increasing the width of the depletion region. This suppresses majority hole transport and limits current to a small leakage current.

Fermi Pinning

At the metal-semiconductor interface, a key phenomenon that can significantly impact contact behaviour is E_f level pinning. This occurs when a high density of interface states, such as defects, dangling bonds, or chemical discontinuities, dominates the charge distribution near the junction. These interface states can trap carriers and effectively fix the E_f at a specific energy, largely independent of the metal's work function. As a result, the expected tunability of the Schottky barrier height through metal selection is suppressed, and the contact may not behave as predicted by ideal theory⁶¹. This pinning effect can hinder performance across a range of devices, including p-n and p-i-n structures, by introducing contact resistance or limiting carrier injection and extraction. To mitigate this, careful interface engineering is essential. This can include the use of surface passivation, insertion of buffer layers, or the selection of contact materials with appropriate electronic alignment to reduce the density of interface states and preserve efficient charge transport.⁶²

2.4 Charge Carrier Behaviour in Semiconductors

Efficient operation of electronic and optoelectronic devices relies fundamentally on the generation, transport, and recombination behaviour of charge carriers. This section provides an overview of key processes affecting carrier dynamics, including excitation, recombination, lifetime, mobility, diffusion length, and the role of trap states.

2.4.1 Carrier Generation, Transport, Recombination

When a photon with energy above the bandgap is absorbed, an electron is excited from the VB to the CB, leaving behind a hole. This creates a free electron-hole pair or, if bound by Coulomb attraction, an exciton. In most semiconductors, low exciton binding energies allow rapid dissociation into free carriers at room temperature.

Charge carriers move through semiconductors via drift and diffusion. Mobility (μ) determines how quickly carriers respond to an electric field ($v_e = \mu E$), while lifetime (τ) is the average time before recombination, inversely related to the recombination rate. These two parameters together define the diffusion length (L), the average distance a carrier can travel before recombining $L = \sqrt{D\tau}$, Where $D = \mu \frac{kT}{q}$. High mobility and long lifetime are essential for achieving long diffusion lengths and efficient charge collection.

Recombination is the process by which electrons and holes are annihilated, releasing energy.

Figure 7 illustrates the main types of recombination:

- **Radiative recombination** (Figure 7 a): An electron falls from the CB to the VB, emitting a photon. This occurs mainly in direct bandgap semiconductors and is desirable in light-emitting devices ⁶⁰.
- **Shockley-Read-Hall (SRH) recombination** (Figure 7 b): Involves trap states within the bandgap, typically due to defects. A carrier is captured by a trap, followed by capture of an opposite carrier, resulting in non-radiative recombination. This is the dominant loss channel in defective materials ⁵⁸. This includes Trap-assisted recombination (Figure 7 c)
- **Auger recombination** (Figure 7 d): A three-body interaction where the recombination energy is transferred to a third carrier, which is excited instead of emitting a photon. It becomes significant at high carrier concentrations.

Minimising non-radiative recombination is crucial for improving device efficiency and can be achieved by reducing trap states, which act as key recombination centres in most semiconductors.

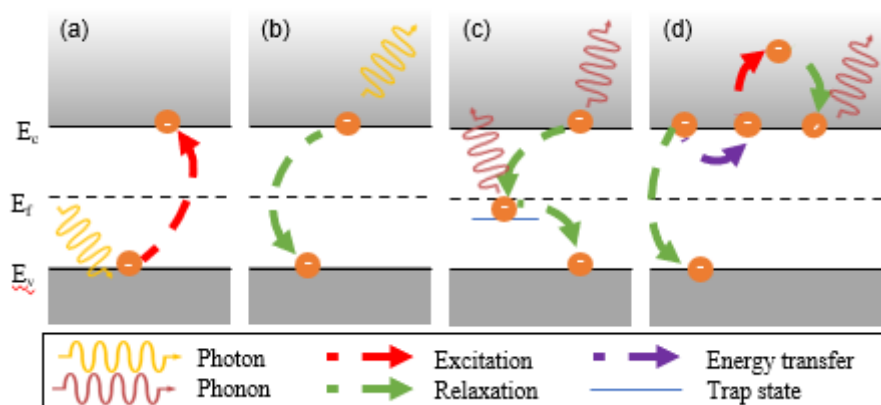


Figure 7 - Illustration of (a) photoexcitation of electrons. (b) Band-to-band radiative recombination. (c) Shockley-Read-Hall non-radiative recombination. (d) Auger non-radiative recombination. ⁵⁷

2.4.2 Trap States

Trap states are localised energy levels within the bandgap that arise from disruptions in the crystal lattice. These states capture charge carriers, reducing lifetime, mobility, and overall device performance. In energetic terms, traps are either shallow or deep. Shallow traps are located near the band edges. Slight lattice distortions or low-energy point defects typically cause them. These traps may temporarily delay carriers but often allow thermal release. Deep traps, on the other hand, are found near the middle of the bandgap. Usually originate from vacancies, interstitials, or chemical

impurities. They are efficient recombination centres and strongly reduce carrier lifetime. These traps are either interfacial or bulk. Interface traps occur at boundaries between different materials. They are caused by incomplete bonding, oxidation, or lattice mismatch, and contribute to surface recombination and instability. Bulk traps are distributed throughout the material. Caused by intrinsic defects during crystal growth or processing. They affect charge transport uniformly across the device. Reducing trap density is essential for enhancing charge collection, stability, and overall device performance.⁵⁷

2.5 All-Inorganic Perovskite Solar Cells

2.5.1 Perovskite Materials: Crystal Structure and Bandgap Engineering

All-inorganic perovskites have the general perovskite ABX_3 structure, where A is a monovalent cation (e.g., Cs^+), B is a divalent metal (e.g., Pb^{2+}), and X is a halide anion (I^- , Br^- , or Cl^-). The structure consists of corner-sharing BX_6 octahedra forming a three-dimensional network, with the Cs^+ cation occupying the cuboctahedra voids between octahedra, as shown in Figure 8 a. The electronic structure is highly sensitive to compositional changes. Halide substitution, such as replacing I^- with Br^- , increases the bandgap, shifting the absorption spectrum toward shorter wavelengths. Similarly, mixed-halide systems such as $CsPbI_2Br$ balance phase stability with optimal bandgap tuning. As mentioned in Chapter 1, Section 3, a key challenge in materials such as $CsPbI_3$ is stabilising the photoactive black phase at room temperature. This phase, while optoelectronically ideal, tends to convert into a yellow non-photoactive phase under ambient conditions. This goes back to the very wide range of ionic radii of the atoms causing an instability in the perovskite crystal. The structural stability of perovskites is quantified by the Goldschmidt tolerance factor (GTF)^{27,46,63–65}:

$$GTF = \frac{r_A + r_X}{\sqrt{2} (r_B + r_X)}$$

where r_A , r_B , and r_X denote the ionic radii of the respective constituents. Ideal cubic perovskite forms when $GTF \approx 1$, while deviations lead to octahedral tilting and phase transitions. In all-inorganic systems, Cs^+ is smaller than organic cations such as MA^+ or FA^+ , which reduces the GTF and predisposes the lattice to distortion. Figure 8 c and d depict the corner-sharing octahedra of the active phase and the edge-sharing configuration of the inactive phase. Similar distortions in the crystal structure alter the overlap of molecular orbitals and consequently modify the bandgap. This factor is what makes $CsPbI_2Br$ more stable than $CsPbI_3$, since their GTF are 0.847 and 0.855, respectively⁶⁶.

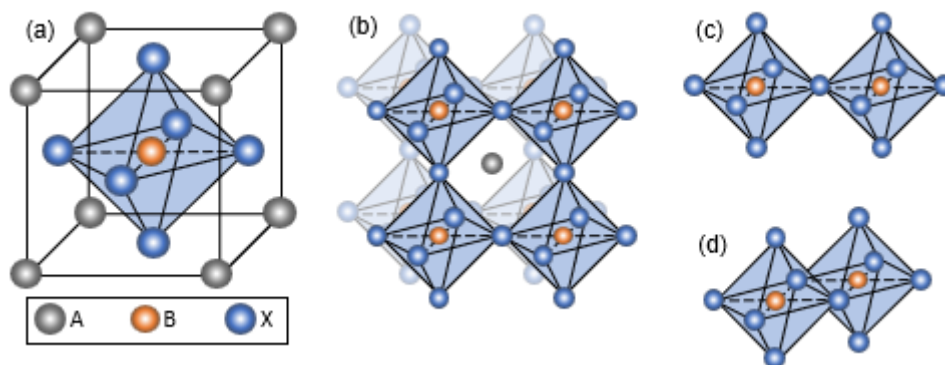


Figure 8 – (a) Unit cell of a perovskite crystal (b) Three-dimensional perovskite lattice (c) Corner-sharing octahedra of the photoactive perovskite phase. (d) Edge-sharing octahedra of a non-perovskite phase.⁵⁷

2.5.2 Phase Stability and Thermodynamics

The unit cell of a crystal is the smallest, three-dimensional building block that when stacked together form the crystal lattice, every mineral has a unique unit cell that is defined by the edge lengths and the angles between them that define the arrangement of atoms, ions or molecules of the crystal. In addition to the interesting GTF of the perovskite material, other factors can cause different crystal structures to be stabilised, including thermal effects, moisture and humidity sensitivity^{67,68}. Inorganic Cs Pb-based perovskites have four main structures: a cubic structure (α -phase), tetragonal (β -phase), orthorhombic (γ -phase and δ -phase). The α , β , and γ phases are of a corner-sharing octahedral structure and are photoactive phases of a brown/black colour. In contrast, the δ -phase has an edge-sharing octahedral structure that forms a 1-dimensional chain-like arrangement, which is photoinactive and exhibits a yellow colour. The difference in crystal structures mostly arises from variations in octahedral tilting and connectivity, which also affects symmetry, bandgap, and electrical and optical properties of the material.^{68–70}

The Pb-I-Pb bond angle in CsPbI_3 varies significantly across its polymorphs, with values of 180° in the α -phase, 164° in the β -phase, $153\text{--}155.6^\circ$ in the γ -phase, and as low as 95.09° and 91.40° in the non-perovskite δ -phase, reflecting the progressive octahedral tilting and symmetry reduction across phase transitions⁷¹. This change in tilt affects the distance and orbital overlapping between the orbitals making up the bandgap (specifically the 6s orbital of Pb and the 5p orbitals of I^-), causing a change in the bandgap and resulting in the optical and electrical properties of the material. Hence, he reported bandgaps of CsPbI_3 phases vary : α - CsPbI_3 exhibits a bandgap of $\sim 1.73\text{ eV}$ ⁷², β - CsPbI_3 shows a theoretical bandgap ranging from 1.68 to 2.06 eV depending on the computational Method, γ - CsPbI_3 has an experimental optical bandgap of $\sim 1.63\text{--}1.75\text{ eV}$ ⁶⁸, and the non-perovskite δ - CsPbI_3 displays a wide bandgap of $\sim 2.82\text{ eV}$ ⁷². In CsPbI_2Br , two reported phases, α and δ , are 1.92 and 2.85 eV^{66,73}.

As well as impacting material properties, the crystal structure also affects phase stability, as the decomposition energies of α , β , and γ -phases of CsPbI₂Br are -0.04, -0.06, and -0.11 eV, making γ -phases less stable than the other phases. The structural degradation does not occur as a direct α -to- δ phase transition. Instead, it follows a temperature-dependent sequence: $\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \delta$, with each step involving a gradual increase in octahedral tilting and a reduction in symmetry. Synchrotron XRD studies confirmed that as the perovskites cool, the structure first transforms into a tetragonal β -phase, then into an orthorhombic γ -phase, before finally reaching the yellow non-perovskite δ -phase⁷⁴. This process initiates at the surface of the crystal and gradually propagates toward the bulk, as observed through *in-situ* imaging studies⁷⁵. Additionally, nanocrystal films show slower phase transition dynamics due to their high surface energy, which helps stabilise the black phase temporarily.

Environmental factors, including moisture, oxygen, light, and heat, strongly influence the degradation of Cs-Pb-based perovskites. Water molecules do not deeply penetrate the lattice but adsorb onto its surface, where they drive the migration of halide ions (I^-/Br^-). This creates halide vacancies that lower the energy barrier for the α -to- δ phase transition, which typically begins at the grain boundaries or surface and propagates inward^{76,77}. Under light, oxygen reacts with water and photogenerated carriers to produce reactive species like superoxides, which then attack the lattice by forming Pb-O bonds and weakening its stability⁷⁷. When both oxygen and moisture are present, water increases the activity of these species, making the α -to- δ transition faster, especially under high humidity and light⁷⁷. Illumination boosts their formation, and temperature changes make things worse by increasing lattice movement and defect activity^{54,77}.

2.5.3 Formation Pathway and Dynamics of the CsPbI₂Br Intermediate

Phase

The crystallisation pathway of CsPbI₂Br is governed by a sequence of early chemical events that begin in solution and proceed through a set of structured, yet metastable, intermediate states. These intermediate phases are not just transient formations, but rather, fundamental to determining the final perovskite film's crystallinity, morphology, and optoelectronic quality. The process initiates when PbX₂ ($X = I^-, Br^-$) is dissolved in solvents such as dimethyl sulfoxide (DMSO) or dimethylformamide (DMF). Due to their strong Lewis basicity, these solvents directly coordinate to the Pb²⁺ centres, forming solvated adducts of the general form PbX₂·DMSO. These complexes play a dual role as they enhance precursor solubility while kinetically slowing down the immediate crystallisation, creating a time window for more controllable intermediate phase formation during spin coating^{78,79}. Upon deposition, these adducts begin to self-assemble into layered structures in which DMSO molecules are intercalated between PbX₆ octahedral chains. The presence of DMSO not only increases the interlayer spacing but also stabilises the lead halide frameworks by holding together the layered structures^{80,81}.

As the wet film begins to dry, Cs^+ ions diffuse into the interlayers of the DMSO- PbX_2 network. This intercalation is energetically favoured due to the small ionic radius of Cs^+ and the expanded spacing between the octahedra layers formed by the DMSO coordination. In doing so, Cs^+ competes with DMSO for binding to PbX_6 edges and weakly coordinated sites, leading to a partial displacement of solvent molecules^{78,81}. The system undergoes a compositional and structural rearrangement, forming a quasi-2D intermediate phase composed of Cs-Pb-X-DMSO structures. Studies such as utilising Fourier Transform Infra-Red Spectroscopy (FTIR) and XRD have confirmed the presence of such phases, with characteristic shifts indicating both Cs incorporation and progressive DMSO removal^{79,80}.

Further solvent evaporation or mild thermal activation facilitates an exchange reaction, where halide ions and Cs systematically displace DMSO. This triggers a reorganisation of the lead halide framework and the emergence of nucleation centres within the metastable intermediate phase. These intermediates, which are often disordered yet chemically templated, are believed to act as structural precursors for the final black-phase perovskite^{78,80,81}. Importantly, the rate of DMSO removal is a key kinetic parameter as slower drying facilitates larger, more coherent nuclei while suppressing non-perovskite secondary phases and pinholes⁷⁸.

2.5.4 Stabilising Photoactive CsPbI_2Br

Stabilising the photoactive black phase of CsPbI_2Br is essential for achieving both high performance and long-term durability in all-inorganic perovskite solar cells. Over the past several years, extensive research has converged on a few stabilisation strategies that varies from compositional and additive engineering to microstructure control and interface design. The most effective phase stabilisation strategies for CsPbI_2Br are cation and halide site doping, additive and defect passivation, morphology tuning through solvent and atmosphere engineering, dimensional and interface modifications, and stress relief via microstructural engineering. Among compositional methods, A-site alkali doping (e.g., K^+ , Rb^+) and B-site incorporation of metals (e.g., Zr^{4+} , Eu^{2+} , In^{3+}) are widely used to reduce defect densities and suppress non-photoactive δ -phase formation. However, optimal doping levels are critical to avoid lattice strain or segregation^{82,83}. Halide ratio tuning through partial iodide-to-bromide substitution further enhances structural stability while tailoring the bandgap⁸⁴. Additive engineering with hydrophobic salts (e.g., TMAI), long-chain ammoniums, and small molecules like HI or DMAI has demonstrated improved crystallinity and ambient phase stability^{84–86}. Passivation agents such as Lewis bases or polymers contribute by reducing surface and grain boundary defects⁸⁴. On the processing side, solvent engineering, anti-solvent treatments, and dynamic hot-air techniques facilitate larger grain sizes and controlled crystallisation, thereby minimising defect-prone boundaries^{84,85,87}. Dimensional engineering using quasi-2D or layered structures enhances moisture resistance and phase stability⁸⁸. Interface engineering, including interlayer modification and surface

reconstruction, addresses interfacial recombination and improves both charge extraction and film robustness ^{84,89}. Finally, suppressing local microstrain between grains via chemical bonding and stress modulation has emerged as a novel route to reinforce phase stability at the lattice level ⁹⁰.

2.5.5 Role of Solvent Engineering, Ratio, and Volatility in CsPbI₂Br Intermediate Phase Formation

The formation of CsPbI₂Br intermediate phases is influenced by solvent properties, particularly coordination strength, volatility, and ratio. These solvent characteristics control the nucleation kinetics, intermediate phase stability, and crystallisation pathway, which in turn dictate the morphology and optoelectronic quality of the final perovskite film. Mixed solvent systems, typically comprising DMF, with stronger coordinating co-solvents such as DMSO or N-methyl-2-pyrrolidone (NMP), are often used to control the crystallisation kinetics. As explained earlier, these cosolvents form strong Lewis's base interactions with Pb²⁺, stabilising intermediate complexes such as PbI₂·DMSO or PbI₂·NMP. This temporary stabilisation delays rapid nucleation and allows for better spatial and temporal control over crystal growth, ultimately enhancing grain uniformity and reducing defects ^{78,91,92}. However, the proportion of these solvents must be carefully optimised. An excessive amount of strongly coordinating solvent can result in slow crystallisation, incomplete conversion during annealing, and the persistence of uncoordinated intermediates, while too little may promote premature nucleation and inhomogeneous grain growth ^{78,91,93}.

The solvent ratio also directly impacts the transformation kinetics of the intermediate phase. For instance, a 3:1 to 9:1 DMSO: DMF ratio has been widely adopted in CsPbI₂Br systems, as this range offers a practical balance between coordination strength and processability and, most importantly, good dissolution of the precursors. At these ratios, intermediate phases such as CsPbI₂Br·DMSO can be reproducibly formed and converted into compact, pinhole-free films upon annealing ^{19,78,92}. The high DMSO content within this optimal window enhances the formation of stable intermediates, thereby promoting larger grain sizes and reducing the density of trap states. However, going beyond this range can hinder complete phase conversion or leave residual solvent complexes that deteriorate device performance ^{92,93}.

Volatility plays an equally critical role in defining the intermediate-to-perovskite transition. Solvents like DMF and γ -butyrolactone (GBL), which exhibit lower boiling points and higher evaporation rates, facilitate rapid immediate nucleation events during spin coating. While this can lead to fast perovskite crystallisation, it often produces small grains and non-uniform morphology if not moderated by a less volatile co-solvent such as DMSO or NMP ^{19,78,91}. These high boiling point solvents slow down the overall solvent evaporation, effectively extending the processing window and promoting gradual

crystallisation. As a result, films processed with low-volatility solvents display enhanced crystal orientation, improved phase purity, and better surface coverage ^{19,93}.

The antisolvent step further compounds these effects by selectively extracting volatile components and triggering a rapid phase transition. By choosing an antisolvent with the appropriate miscibility and volatility, such as chlorobenzene or diethyl ether, the weakly bound DMF is efficiently removed. At the same time, the DMSO-coordinated intermediate remains momentarily stabilised. This results in a fast supersaturation event that facilitates a controlled nucleation, followed by the formation of a stable intermediate phase ^{19,92,93}. However, if the primary solvent system is too rich in low-volatility solvents, the antisolvent may become ineffective in initiating proper nucleation, leading to incomplete film formation or the entrapment of excess solvents in the film matrix ^{92,94}. Conventional antisolvents often fail to effectively extract excess DMSO, as higher DMSO ratios are required to dissolve Cs precursors, ultimately leading to poor film formation. This limitation has driven the development of antisolvent-free fabrication strategies.

Altogether, solvent engineering emerges as a strategic tool to modulate intermediate phase chemistry and crystallisation behaviour. By tuning the coordination strength, volatility, and relative ratios of solvents nucleation pathways and film evolution dynamics can be tailored. This approach not only improves phase stability and reduces defect densities but also enables scalable fabrication techniques such as blade coating or slot-die printing, where extended processing windows and controlled solidification are essential ^{19,78,93,94}. Moreover, ongoing efforts to incorporate greener and less toxic solvent systems highlight the environmental and industrial relevance of solvent engineering in the development of stable, high-performance CsPbI₂Br perovskite solar cells ^{19,78,94}.

2.5.6 Void Formation in CsPbI₂Br Films

The way CsPbI₂Br perovskite films crystallize plays a major role in their final structure and performance. When crystallization happens at low temperature (room temperature or mild heating), it is mostly controlled by the solvents rather than by thermal energy. Since ion movement is limited under these conditions, structural rearrangement and defect healing are also limited. After nucleation, the grains grow through a process called Ostwald ripening, where small grains dissolve and re-deposit onto larger ones. This helps reduce grain boundaries, which is good for charge transport. However, if grain growth is too aggressive, it can lead to uneven grain sizes or even voids. To prevent this, additives or surface ligands are often used to control the ripening process and improve uniformity ⁹⁵. During spin coating, the perovskite solution is spread into a thin layer while solvents like DMF and DMSO begin to evaporate. Evaporation happens faster at the top of the film because it's exposed to air, while the bottom evaporates more slowly as it's closer to the substrate. This creates a vertical gradient in solvent content, which affects how the film crystallises ^{95,96}. In DMSO-rich systems, the top

layer reaches supersaturation and starts to crystallize first. This creates a thin solid “skin” at the surface, and crystallization then moves downward through the film. While this top-down process can help align grains vertically (which is good for out-of-plane charge transport), it can also trap solvent or unreacted precursors underneath the surface crust. This can lead to uneven grain growth, secondary phases, and voids ^{96,97}. Voids are a common issue in CsPbI₂Br films and can severely affect device performance by disrupting charge transport and creating weak points in the structure. These voids can form for different reasons and in different parts of the film ^{98,99}. They are usually grouped into four main types:

- **Interfacial voids:** Found between the perovskite and underlying layer, often due to poor wetting or delayed crystallisation ^{98,99}.
- **Intragranular voids:** Found inside grains, often caused by trapped solvent or shrinking during solidification ⁹⁸.
- **Intergranular voids:** Found between grains when they don’t fully merge ^{98,100}.
- **Surface pinholes:** Visible holes at the surface, caused by de-wetting or rapid crystallisation ⁹⁹.

There are several mechanisms that can lead to the formation of voids. One is trapped solvent, where a solid crust forms on the surface while solvent remains underneath. As the solvent evaporates, it can create blisters or internal cavities ^{96,98}. Another cause is poor grain merging, which happens when grains do not fully coalesce, leaving small voids between them ¹⁰⁰. Volume shrinkage can also lead to voids; as the material transitions from a solvated state to a solid, it shrinks. If this shrinkage occurs unevenly, internal stress can create micro voids ⁹⁸. Additionally, gas release during annealing can cause voids. Leftover precursors may decompose and release gases, and if these gases cannot escape, they form voids inside the film ^{99,100}. These are some common causes, but void formation is not limited to just these mechanisms. Although these are some contributing mechanisms, void formation is not exclusively due to them. This thesis will explore an additional means in which voids are filled.

2.5.7 Role of Oxygen and Air-Processing in the Phase Stability of CsPbI₂Br

CsPbI₂Br exhibits a unique interaction with ambient oxygen that can either induce degradation or enhance phase stability depending on processing conditions. While oxygen is commonly associated with degradation mechanisms in perovskites, particularly in the presence of light and moisture, recent studies have demonstrated that under controlled conditions, oxygen can play a beneficial role in stabilising the active phase of CsPbI₂Br. The key to this stability lies in the formation of Pb-O bonds. During air-processing, oxygen atoms interact with undercoordinated Pb²⁺ ions to form Pb-O bonds

and stop them from being trap states. This passivation function significantly suppresses the transition from the photoactive α -phase to the non-photoactive δ -phase^{77,77}. It does not only responsible for enhanced phase stability but also improves photovoltaic performance and reduces hysteresis by lowering trap-state density⁷⁷. Films prepared under dry air (relative humidity, RH < 15%) demonstrate enhanced crystallinity and phase retention compared to those fabricated entirely in nitrogen⁷⁷. Furthermore, oxygen-induced passivation is more effective when oxygen atoms are involved, as atomic oxygen binds more strongly to halide vacancies and surface Pb sites¹⁰¹. Dry-air processing allows for the dissociation of O₂ into reactive oxygen atoms, leading to deeper passivation, lower defect densities, and improved long-term performance^{77,101}. This mechanism supports the use of ambient fabrication environments with controlled humidity and oxygen content for scalable and stable PSC production^{77,102}.

Humidity plays a secondary role. Trace moisture stabilises reactive O₂⁻ species, which further enhance the passivation of Pb²⁺ and facilitate additional Pb-O bond formation. This stabilises the perovskite structure even under moderate humidity (30-45% RH), even though higher moisture levels are known to promote halide vacancy formation and α -to- δ phase transitions^{76,77}. Importantly, CsPbI₂Br films processed in air exhibit superior long-term stability in both low and moderate humidity environments compared to their nitrogen-processed counterparts⁷⁷. Moisture promotes halide migration to the film surface, creating halide vacancies and lowering the energy barrier for α - δ phase transitions⁷⁶. However, the presence of Pb-O bonds formed early in the film formation stage prevents the propagation of the δ -phase. This explains the counterintuitive result that air-processed CsPbI₂Br can be more stable than films formed under nitrogen^{76,77}.

2.5.8 The Role of Strain and Microstrain in Phase Stability of Inorganic Perovskites

Strain and microstrain is an intrinsic mechanical feature that influences the structural and phase stability of inorganic halide perovskites, such as CsPbI₂Br and CsPbI₃. In these materials, even slight distortions in the lattice or at grain boundaries can trigger phase transitions, accelerate degradation, or disrupt charge transport. The issue is especially problematic in all-inorganic compositions since they typically require higher processing temperatures for full crystallisation, thus experiencing more intense thermal mismatch strain compared to organic-inorganic perovskites¹⁰³. This strain emerges due to differences in thermal expansion coefficients (TECs) between the perovskite layer and adjacent layers (e.g. substrates or charge transport materials)^{103,104}. Notably, CsPbI₂Br exhibits one of the highest TECs among perovskites, making it highly susceptible to residual stress during cooling from annealing temperatures¹⁰³.

The thermal strain formed during film cooling leads to tensile stress in the perovskite layer, particularly as it transitions from cubic to tetragonal phases ¹⁰⁵. This transition involves octahedral tilting and unit cell distortion, which contributes to lattice asymmetry and strain accumulation. If not properly relieved, this residual tensile strain can exceed 50 MPa, thus acting as a major driver for instability, cracking, and eventual device failure ¹⁰⁶. Strain also impacts optoelectronic performance. It is now established that tensile strain not only facilitates defect formation but also increases non-radiative recombination by lowering the energy barrier for ion migration ^{106,107}. These effects are particularly pronounced in mixed-halide perovskites, where compositional heterogeneity introduces local lattice mismatches and residual strain that degrade long-term stability ^{108,109}. As a result, strategies such as strain engineering, additive passivation, and pre-strain compensation have become essential for achieving phase-stable, high-performance all-inorganic perovskite solar cells ¹⁰⁷.

Microstrain, the local variation in lattice spacing typically at grain boundaries or defect sites, is another factor affecting phase stability. Microstrain in CsPbI₂Br films promotes lattice distortion under environmental stressors like humidity, accelerating the transformation to the non-perovskite δ -phase ⁹⁰. This transformation is particularly problematic because the yellow δ -phase is thermodynamically favoured at ambient conditions. By contrast, reducing microstrain via gradient cooling, defect healing via a gradient cooling strategy ⁹⁰, hot-air processing ¹¹⁰, or optimised additive incorporation ⁹⁰ can enhance lattice coherence and suppress such transitions. For example, SEM and XRD analyses show that gradient-cooled and hot-air-processed films exhibit narrower diffraction peaks, indicating reduced microstrain and improved crystallinity ^{110,111}.

Chapter 3: Experimental Methods

3.1 Thin Film Deposition

All devices were fabricated on indium-tin oxide coated glass substrates (ITO, $15\ \Omega\ \text{sq}^{-1}$). Before deposition, the substrates were ultrasonically cleaned in deionised water, acetone, and isopropanol for 15 minutes in each solvent. After cleaning, the substrates were dried under a nitrogen stream and treated with UV-ozone for 15 minutes to remove residual organic contaminants and improve surface wettability.

The hole transport layer (HTL) was formed using [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz), purchased from TCI (98.0%), dissolved in ethanol at 1 mM concentration. The solution was spin-coated at 3000 rpm, with an acceleration of 1500 rpm/s, for 30 seconds, followed by thermal annealing at 100 °C for 10 minutes. The perovskite precursor solution was prepared by mixing CsI (99.9% Sigma-Aldrich), PbI_2 (99.99%, TCI or Thermo Fisher Scientific), and PbBr_2 (>99.0%, Thermo Fisher) in a 2:1:1 molar ratio. Unless otherwise specified, the solution concentration was 1 M, and the solvent mixture used was a 1:9 volume ratio of DMF to DMSO and the solution is spin coated at 4000 rpm for varying durations (As specified in the following chapters then annealed at 160°C. All solvents were anhydrous and obtained from Sigma-Aldrich. Spin-coating conditions varied depending on the experiment and are specified in each chapter accordingly. For the electron transport layers (ETLs), C_{60} (Ossila, >99.5%) and bathocuproine (BCP) (Lum tec, >99.5%) were sequentially deposited by thermal evaporation under high vacuum (5×10^{-6} mbar) to final thicknesses of 30 nm (C_{60}) and 8 nm (BCP). A 100 nm layer of silver (Ag) was then thermally evaporated to serve as the top electrode. A shadow mask was used during the BCP and Ag deposition steps to define the device area, resulting in a fixed active area of 0.045 cm² for all measured pixels. The device architecture studied is illustrated in Figure 9.

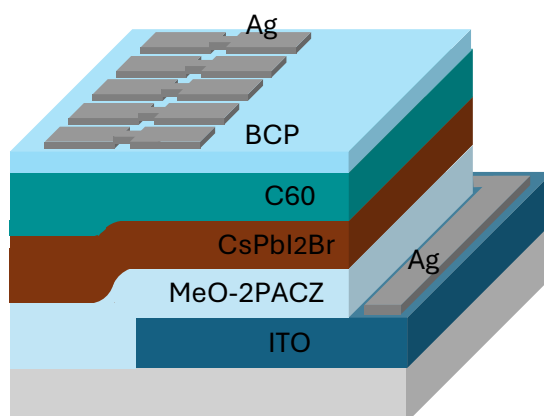


Figure 9 – Illustration of p-i-n device architecture used in this study.

3.2 Structural, Compositional & Chemical Characterisation

3.2.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive technique that probes the structural properties of crystalline materials by irradiating them with incident X-rays and detecting the angles and intensities of the diffracted beams. By analysing the resulting diffraction pattern, information about the atomic arrangement, lattice parameters, and microstructural features can be extracted. In this study, grazing-incidence XRD (GIXRD) was also employed to enhance surface sensitivity and enable depth-resolved structural analysis by varying the incident angle. Lower angles confine the penetration depth to near-surface regions, while higher angles progressively access deeper layers, allowing the structural evolution throughout the film thickness to be mapped. Key information can be extracted from the position, width, and intensity of the diffraction peaks. XRD peak positions are determined by the spacing between atomic planes in a crystal, which is determined by Bragg's Law (Equation 1):

$$n\lambda = 2d \sin\theta \quad \text{Equation 6}$$

Where λ is the X-ray wavelength (1.5406 Å for Cu K α radiation), d is the interplanar spacing, and θ is the angle of incidence. Shifts in peak positions and relative intensities are related to the structure and composition of the material. When considering discrete families of materials, such as the perovskite systems studied here, shifts in peak position can be correlated with doping or the presence of macroscopic (uniform) strain. Such strain can be quantified relative to a strain-free reference material using:

$$\varepsilon = \frac{d-d_0}{d_0} = \frac{\sin \theta_0}{\sin \theta} - 1 \quad \text{Equation 7}$$

Where θ_0 corresponds to the unstrained peak position and d_0 the interplanar spacing of the unstrained reference. A shift to lower 2θ indicates tensile strain (lattice expansion), while a shift to higher 2θ indicates compressive strain (lattice contraction). In contrast, microstrain refers to local, non-uniform distortions in the lattice caused by defects, dislocations, or heterogeneous stress. Unlike macroscopic strain, microstrain does not shift the peak position; instead, it leads to peak broadening. It can be estimated from the full width at half maximum (FWHM) of the peak using the Williamson-Hall method:

$$\beta \cos \theta = \frac{k\lambda}{L} + 4\eta \sin \theta \quad \text{Equation 8}$$

Where β is the peak broadening in radians (after instrumental correction), L is the crystallite size, η is the microstrain, and k is the shape factor (typically 0.9). A broader peak may thus reflect either smaller crystallites or higher microstrain, or both. It is important to note here that we have calculated both the standard FWHM, which is the spectral width measured at 50% of the peak intensity, and the effective

FWHM, which is simply obtained by dividing the total area under the peak by its maximum height, giving an equivalent width that accounts for peak asymmetry.

Additionally, the intensity of each diffraction peak reflects the degree of crystallinity and preferred orientation. High intensity generally indicates strong alignment along specific crystallographic directions, which is especially relevant for assessing film texture and phase purity.

Thin-film XRD measurements were performed using a PANalytical Empyrean diffractometer (Cu K α , $\lambda = 1.5406 \text{ \AA}$), configured for grazing-incidence scans at multiple angles to probe structural variations with depth. During the early stages of this work, it became apparent that conventional XRD sample holders and encapsulation approaches were insufficient to prevent air exposure of CsPbI₂Br films during intermediate processing stages, particularly during the pre-anneal hold step where the films are highly sensitive to moisture and oxygen. Multiple sealing and encapsulation strategies were tested, but residual air exposure led to inconsistent and misleading phase observations. To overcome this limitation, a glovebox-integrated XRD system was utilised, and the measurement protocol was adapted to enable truly air-free structural characterisation without the need for encapsulation or sample transfer. This approach allowed repeated time-resolved scans to be performed directly during the hold process and thermal treatment, ensuring that the structural evolution observed reflects the intrinsic behaviour of the films rather than artefacts introduced by environmental exposure. This measurement strategy was essential for the reliable interpretation of the in-situ XRD results presented in this thesis. To monitor real-time changes during thermal treatment, *in-situ* XRD was carried out under a nitrogen atmosphere using a Rigaku MiniFlex600 (Cu K α , $\lambda = 1.54059 \text{ \AA}$) in powder geometry. The in-situ XRD was performed by Sarah McKinney from Nuria Tapia Ruiz's Group. This configuration was particularly important for the air-sensitive measurements described in Chapter 4, where the glovebox integration enabled reliable tracking of intermediate phase evolution.

For data processing, the background was removed from the XRD scans (where required for low-intensity data) using *MATCH!* software. A custom MATLAB script was then used for automated peak fitting. The approximate peak positions were specified in advance, and each peak was analysed using a piecewise asymmetric pseudo-Voigt (APV) model. In this formulation, the peak is divided into two half-profiles (left and right of the peak centre). Each half is described by a single width parameter shared between the Gaussian and Lorentzian contributions and an independent Gaussian-Lorentzian mixing factor, enabling the model to reproduce asymmetric peak shapes with a minimal but flexible parameter set.

Mathematically, the APV function is given by:

$$f(x) = \begin{cases} A \cdot \left[\eta_L \cdot \frac{1}{1 + \left(\frac{x-x_0}{s_L}\right)^2} + (1 - \eta_L) \cdot e^{-\ln(2) \cdot \left(\frac{x-x_0}{s_L}\right)^2} \right], & \text{if } x < x_0 \\ A \cdot \left[\eta_R \cdot \frac{1}{1 + \left(\frac{x-x_0}{s_R}\right)^2} + (1 - \eta_R) \cdot e^{-\ln(2) \cdot \left(\frac{x-x_0}{s_R}\right)^2} \right], & \text{if } x \geq x_0 \end{cases} \quad \text{Equation 9}$$

where A is the peak amplitude, x_0 is the peak centre, s_L and s_R are the left and right widths (used in both Gaussian and Lorentzian contributions), and η_L and η_R are the Gaussian-Lorentzian mixing factors on the left and right sides of the peak, respectively. This formulation was inspired by prior work on asymmetric peak modelling in spectroscopy, by Hansen *et al.*¹¹², and extended here to allow full piecewise asymmetry tailored to each peak and scan in diffraction data.

Before fitting, the background-corrected signal was smoothed using a Savitzky-Golay filter (order 9, frame 35) to suppress noise. For quality control, each scan was plotted showing the raw, smoothed, and fitted curves, as well as the total fitted profile and the residual (data - fit), to ensure no systematic deviations remained. The full MATLAB script is provided in the Appendix I.

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Attenuated total reflectance Fourier transform infra-red spectroscopy (ATR-FTIR) was used to study the surface chemistry of the films by identifying specific chemical bonds and functional groups. In this method, an infrared beam is directed into a high-refractive-index crystal (typically diamond), where it reflects internally at the point of contact with the sample. Although the beam does not pass into the sample, it generates a short-range field that reaches slightly beyond the surface (only a few microns deep). This surface-confined interaction allows ATR-FTIR to probe the chemical composition of thin films without needing transmission through the full thickness. The resulting spectrum shows how much of the infrared light is absorbed at different wavelengths, each corresponding to the vibrational motion of a specific bond (such as stretching or bending). The position of each absorption band reveals the type of chemical bond present, while the intensity gives a relative idea of its concentration. Shifts in peak position or changes in shape can indicate chemical changes at the surface: such as hydrogen bonding, degradation, or coordination with additives. The method is especially useful for detecting residual solvents, surface-bound species, and decomposition products in perovskite films. In this study, ATR-FTIR measurements were performed using an Agilent Cary 630 FTIR spectrometer (funded by the chemistry department), which was placed inside a nitrogen-filled glovebox to prevent exposure to ambient conditions. This allowed chemical analysis to be performed under inert conditions, preserving the native state of the films.

3.2.3 X-ray Photoelectron Spectroscopy (XPS) and Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS)

X-ray Photoelectron Spectroscopy (XPS) is a surface-sensitive technique used to determine the elemental composition and chemical environment of atoms within the top few nanometres of a material. When the sample is exposed to X-rays, electrons from inner atomic orbitals can absorb sufficient energy to escape the atom. These emitted photoelectrons are collected and analysed to determine their kinetic energy. From this, the binding energy of the electron is calculated using:

$$E_{Binding} = h\nu - E_{Kinetic} - \phi \quad \text{Equation 10}$$

Where $h\nu$ is the photon energy, $E_{Kinetic}$ is the measured kinetic energy of the electron, and ϕ is the spectrometer's work function. Each atomic orbital has a characteristic binding energy, and because these values are element- and oxidation-state specific, XPS can be used to identify which elements are present and how they are bonded. In perovskite films, for example, the Pb 4f signal shifts depending on whether lead is present in the +2 oxidation state or as metallic Pb⁰. Similar chemical shifts in the Br 3d and I 3d peaks can indicate halide loss, surface degradation, or interaction with additives.

Angle-resolved X-ray photoelectron spectroscopy (ARXPS) was used to probe the depth distribution of elements and chemical states in the perovskite films with enhanced surface sensitivity. ARXPS measurements were performed using the same Thermo Fisher K-Alpha⁺ system described above, with the take-off angle measured from the surface normal varied between 10° and 90°. By systematically increasing the take-off angle, the sampling depth was reduced, enabling a qualitative depth profile of the chemical composition and oxidation states without sputtering. All spectra were calibrated to the adventitious carbon C 1s peak at 284.8 eV to correct for any charging effects. For each angle, spectra were first corrected by applying a linear baseline subtraction to remove background contributions.

The data were collected using the Scanning ESCA Microprobe PHI 5000 VersaProbe from ULVAC-PHI at National Chung Hsing University, Taiwan, through Prof. Chieh-Ting Lin's group with the help of Yun Shan Li (Stella).

Quantification and peak deconvolution were performed using KherveFitting software. Each core-level region was fitted using a mixed Gaussian-Lorentzian (GL) line shape, specifically a Voigt-like function, which accounts for both instrumental broadening (Gaussian) and lifetime broadening (Lorentzian). Doublet splitting was constrained to the known spin-orbit splitting energies and area ratios for each

element (e.g., Pb 4f_{7/2}:Pb 4f_{5/2} = 4:3). The fitting parameters included peak position, full width at half maximum (FWHM), and peak area.

3.2.4 Kelvin Probe (KP) and Atmospheric Pressure Photoelectron Spectroscopy (APS)

Kelvin Probe (KP) was used to determine the work function of the perovskite films. In this technique, the contact potential difference between the sample and a vibrating reference probe is measured to determine the work function. The WF is obtained from the measured contact potential difference, which directly reflects the energy difference between the Fermi level and the vacuum level. This value reflects the energy required to move an electron from the Fermi level to the vacuum level. It is determined by calibrating the probe work function and calculating the sample's WF from the voltage difference. The energy difference VBM is extracted using Ambient pressure photoelectron spectroscopy (APS), where the onset of photoemission corresponds to the top of the valence band. By combining this with the optical band gap, the whole energy level structure of the material can be constructed. A slight negative bias is applied during the measurement to improve the detection of low-energy electrons and ensure accuracy in both work function and VBM analysis.

The KP and APS use was APSO4 from KP Technology the measurements were performed by Yun Shan Li(Stella) and Wei Jia Qui (Garry) from Prof. Chieh-Ting Lin's group.

3.3 Morphological Characterisation

3.3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was employed to investigate the surface and cross-sectional structure and morphology of the perovskite films. In this technique, a focused beam of high-energy electrons is rastered across the surface of a specimen. As these electrons interact with the sample several types of detectable signal can be generated, for imaging purposes secondary electrons (SE) and backscattered electrons (BSE) are primarily collected. SE are low energy, typically < 50 eV, electrons emitted from the surface and are used to produce detailed topographic images. Backscattered electrons are generated as a result of elastic scattering, where the kinetic energy of the beam is preserved; consequently, these will be of higher energy, > 50 eV and consequently yield energy from deeper in the sample relative to SE. Top-view images were collected to evaluate the grain size, film-coverage, and surface uniformity of the perovskite films. Cross-sectional images were used to examine the layer thicknesses and the quality of the interfaces between device layers.

To further assess the morphology of buried interfaces, a novel image analysis technique was developed to quantify the formation of voids. In this method, 15 images were collected for each sample and analysed using segmentation to isolate and measure void regions. The total void area in each image was normalised to the fixed imaging area of $\sim 128 \mu\text{m}^2$ and treated as a single data point. This enabled comparison of both total void coverage and void size distribution across samples. All SEM images were acquired using a Zeiss Sigma 300 Gemini 1 SEM under a set of identical imaging conditions, *i.e.* fixed accelerating voltage, aperture, contrast, brightness, resolution, and scan speed, ensuring comparability across all datasets. The resolution used was 2048×1536 , the accelerating voltage was 2.5 kV with a $30 \mu\text{m}$ aperture, and a working distance of around 4 mm. The instrumental scan speed was set to 6, and brightness and contrast were around 50% and 22%, respectively. To expose the buried interface for SEM analysis, a thin layer of epoxy was first deposited onto the perovskite film surface. A glass microscope slide was then gently placed on top to spread the epoxy uniformly across the film. The epoxy was cured under UV illumination to ensure strong adhesion between the epoxy and the film surface. After curing, the glass slide was slowly peeled away from the substrate such that the epoxy remained attached to the slide while adhering to the film. This process mechanically lifted the perovskite layer from the substrate, thereby exposing the buried interface. The exposed interface was subsequently imaged using SEM.

3.4 Electrical Characterisation

3.4.1 Current area-voltage (J-V)

Current area-voltage (J-V) measurements were used to evaluate the performance of devices under dark and illuminated conditions. These measurements provided the key photovoltaic parameters: open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), power conversion efficiency (PCE), as well as series resistance (R_s) and shunt resistance (R_{sh}). Under illumination, the absorption of photons generates electron-hole pairs, which are separated by the built-in electric field of the device, producing a photocurrent (J_{ph}). The output current can be described by the superposition of the dark diode current and the light-generated current:

$$J(V) = J_0 \left(e^{\frac{qV}{nkT}} - 1 \right) - J_{ph} \quad \text{Equation 11}$$

At open-circuit conditions ($J = 0$), this leads to a maximum voltage (V_{oc}), which corresponds to the separation between the quasi-Fermi levels. At short-circuit conditions ($V = 0$), the current reaches its maximum value (J_{sc}). The point at which the product of current and voltage is highest defines the maximum power point (MPP). The fill factor (FF) describes how square the J-V curve is:

$$FF = \frac{V_{MPP} J_{MPP}}{J_{sc} V_{oc}} \quad \text{Equation 12}$$

The power conversion efficiency (PCE), η , is then given by:

$$\eta = \frac{FF V_{OC} J_{SC}}{P_{in}} \quad \text{Equation 13}$$

Where P_{in} is the power of the incident light. These values were directly extracted from the measured J-V.

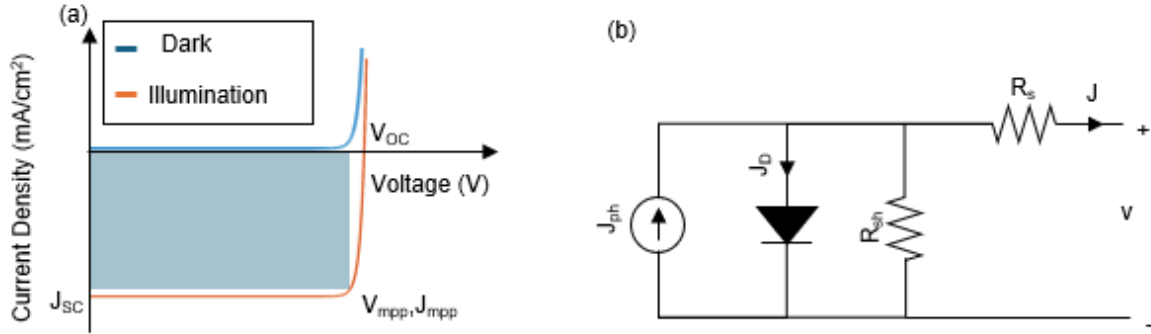


Figure 10 - (a) J-V curve under dark conditions (blue) and illumination (orange) of an ideal solar cell (b) Equivalent electrical circuit of a solar cell.⁵⁷

We also performed dark J-V scans, represented in Figure a, to study recombination and extract parasitic resistances. The ideal diode behaviour follows $J(V) = J_0 e^{\frac{q(V+J R_s)}{nkT}} - J_{ph}$

Equation 11, where $J_{ph}=0$. In real devices, however, R_s and R_{sh} must be included as shown by the equivalent electrical circuit of a solar cell (Figure b). The full equation becomes:

$$J(V) = J_0 \left(e^{\frac{q(V+J R_s)}{nkT}} - 1 \right) - J_{ph} + \frac{V+J R_s}{R_{sh}} \quad \text{Equation 14}$$

Here, R_s causes voltage losses due to resistive components in the device layers or contacts, while R_{sh} captures current leakage through alternative paths, such as pinholes. Both were extracted by fitting the dark J-V response. Finally, to understand the dominant recombination pathway, we performed light-intensity-dependent J-V scans. By plotting V_{oc} as a function of the logarithm of light intensity, we extracted the ideality factor (n), which provides insights into the recombination mechanism. An ideality factor near 1 indicates bimolecular recombination, whereas a value near 2 suggests trap-assisted Shockley-Read-Hall (SRH) recombination:

$$V_{OC} = \frac{nkT}{q} \ln \left(\frac{J_{ph}}{J_0} + 1 \right) \quad \text{Equation 15}$$

J-V measurements were performed using a Keithley 4200 Source-Measurement Unit at a scan rate of 25 mV s^{-1} , under AM 1.5G illumination (100 mW cm^{-2}) provided by an Oriel solar simulator with a Xenon lamp. The light intensity was calibrated using a certified silicon reference cell. All measurements were carried out in a nitrogen-enclosed chamber, scanning from -0.5 to +1.3 V. Light-intensity-dependent J-V measurements were performed by varying the illumination using a set of neutral density (ND) filters. The intensity under each filter was measured and calibrated using the same certified silicon reference cell.

3.4.2 External Quantum Efficiency (EQE)

External quantum efficiency (EQE) measurements were performed to assess device efficiency in converting incident photons into collected charge carriers across different wavelengths. The EQE spectrum provides wavelength-resolved insight into the device's photo-response and helps identify parasitic absorption or spectral losses. EQE, illustrated in Figure 11, is defined as the ratio of the number of collected charge carriers to the number of incident photons at each wavelength

$$EQE(\lambda) = \frac{\text{Collected electrons per second}}{\text{Incident photons per second at } \lambda} \quad \text{Equation 16}$$

It is usually expressed as a percentage and measured over the relevant solar spectrum. A high EQE across this range indicates good absorption and charge collection efficiency, while dips in the spectrum can point to reflection, parasitic absorption, or recombination losses. By integrating the EQE spectrum over the AM1.5G solar spectrum, the expected J_{SC} can be calculated:

$$J_{SC} = q \int EQE(\lambda) \cdot \Phi(\lambda) d\lambda \quad \text{Equation 17}$$

where $\Phi(\lambda)$ is the incident photon flux ($\text{photons} \cdot \text{s}^{-1} \cdot \text{cm}^{-2} \cdot \text{nm}^{-1}$) and q is the elementary charge. This calculated J_{SC} is often compared with the J_{sc} from J-V measurements as a consistency check. The EQE measurements were performed using PVE300 Bentham photovoltaic EQE setup

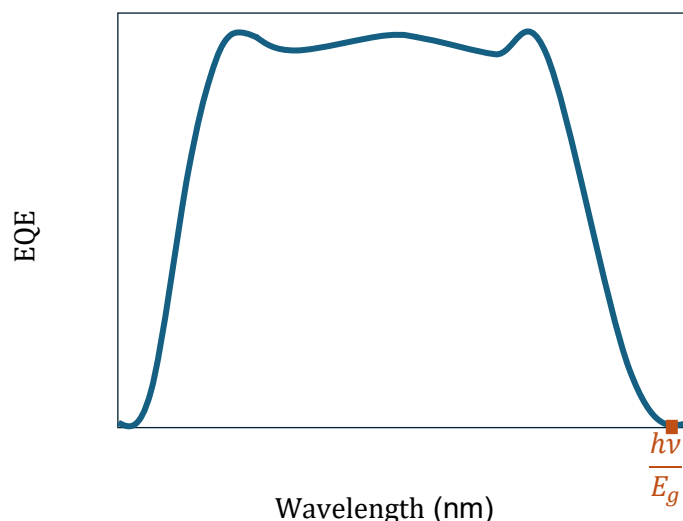


Figure 11 – Schematic illustration of a typical EQE plot, the wavelength corresponding to the bandgap is highlighted ($h\nu/E_g$).

3.4.3 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was used to investigate the internal electrical behaviour of the devices by applying a small AC signal over a range of frequencies in the dark. The resulting response was plotted as a Nyquist plot (Figure 12), where the imaginary part of the impedance ($-Z''$) is plotted against the real part (Z'). In perovskite devices, Nyquist plots typically display one or more semicircles, each representing distinct physical processes. The high-frequency arc typically relates to charge transport and contact resistance, while the low-frequency arc can reveal interfacial behaviour or ionic motion. These responses were analysed by fitting the data to equivalent circuits consisting of resistive and capacitive elements, which allowed us to extract parameters such as series resistance, charge transfer resistance, and interfacial capacitance.

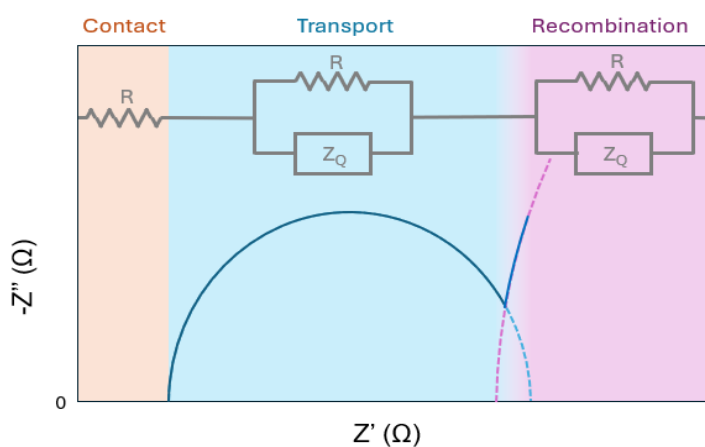


Figure 12 – Illustration of Nyquist plot showing the equivalent electrical elements of contact, transport and recombination losses.

All EIS measurements were carried out using a CHI600E electrochemical workstation. Nyquist plots were collected over a frequency range of 2 MHz to 1 Hz, using an AC amplitude of 0.548 mV. Data analysis and equivalent circuit fitting were performed using Gamry *EIS300 EIS* software. The EIS were performed by Amanz Azaden and Kunrou Fu from Prof. Saif Haque group.

3.5 Optical Characterization

3.5.1 Ultraviolet-Visible Spectroscopy - (UV-Vis)

Ultraviolet-visible spectroscopy (UV-Vis) was used to study the optical absorption behaviour of the perovskite films by measuring the amount of light transmitted through the sample. A beam of light with intensity I_0 is directed at the sample, and the transmitted light intensity is detected. The absorbed (A) is calculated using:

$$A = -\log\left(\frac{I}{I_0}\right) = -\log(T) \quad \text{Equation 18}$$

To estimate the optical bandgap, we applied the Tauc method, which is based on the Beer-Lambert law, $\alpha = \frac{A 2.303}{l}$, where α is the absorption coefficient and l is the film thickness. The bandgap E_g was extracted by plotting the Tauc equation:

$$(\alpha h\nu)^\gamma = (h\nu - E_g) \quad \text{Equation 19}$$

Where h is Planck's constant, ν is the frequency of light, γ reflects the nature of the electronic transition, where $\gamma=2$ corresponds to a direct allowed bandgap, and $\gamma=0.5$ corresponds to an indirect allowed bandgap, and $h\nu = \frac{hc}{\lambda}$, where c is the speed of light, and λ is the wavelength. By extrapolating the linear region of the Tauc plot to intersect the photon energy axis, we obtained the bandgap E_g . The onset of absorption was also used to cross-check the bandgap values. All absorption spectra were collected using an Agilent Cary 60 UV-Vis spectrometer in the range of 300-900 nm.

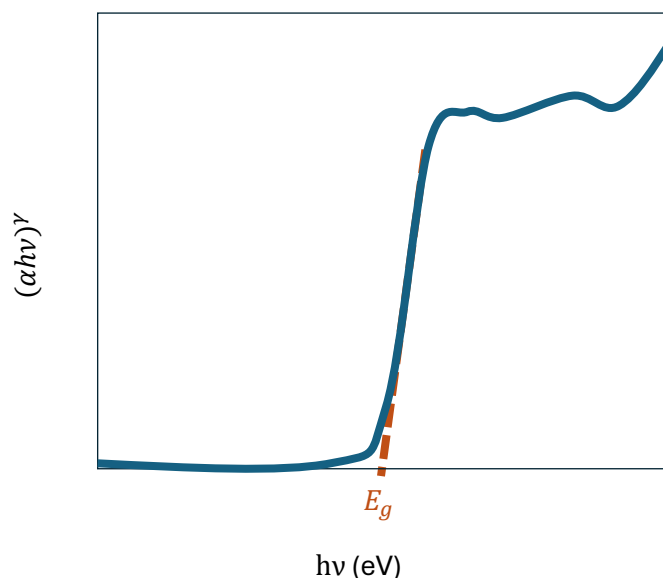


Figure 13 – Schematic illustration of a typical Tauc plot, the tangent to the absorption onset is used to determine the bandgap.

3.5.2 Steady-State Photoluminescence (PL)

Steady-state photoluminescence (PL) was used to investigate the radiative recombination behaviour of the perovskite films. In this technique, the sample is excited with a fixed wavelength light source, and the emitted light is collected and analysed as a function of wavelength. The resulting spectrum provides insight into the electronic structure and recombination processes within the material. The PL peak position reflects the energy gap between the conduction band and valence band. Shifts in this position can indicate changes in crystallographic phase, compositional variations, or strain. The PL intensity serves as an indirect indicator of non-radiative losses: higher intensity typically suggests reduced trap-assisted recombination and improved film quality. All steady-state PL measurements were performed using a Cary Eclipse Fluorescence Spectrometer with an excitation wavelength of 404 nm. For *in-situ* PL measurements (unless otherwise specified), a setup was built using USB2000 Ocean Optics Spectrometer. For the PL scans in the Warm-air-assisted Deposition project, measurements at the front and back of the samples were performed using the FLS1000 by Nicole Dong from Thomas Macdonald's group.

3.5.3 Time-Correlated Single Photon Counting (TCSPC)

Time-correlated single photon counting (TCSPC) was employed to perform time-resolved photoluminescence (TRPL) measurements, enabling the investigation of charge carrier recombination dynamics in the perovskite films. This method records the time delay between a short laser excitation pulse and the detection of a single emitted photon, repeated over many cycles to generate a precise decay profile. In TCSPC, a pulsed laser excites the sample periodically. Each time

a photon is emitted, its arrival time relative to the laser pulse is detected by a highly sensitive photon detector. The system only records one photon per cycle, ensuring high timing accuracy. After many excitation-emission events, the instrument builds a histogram of photon arrival times, which reflects the photoluminescence decay curve of the material. This technique offers high temporal resolution, making it suitable for analysing fast recombination processes in thin-film semiconductors. For samples deposited on glass, the decay is modelled using a biexponential function:

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad \text{Equation 20}$$

Where $I(t)$ is the PL intensity at time t , A_1 and A_2 are the amplitudes, and τ_1 and τ_2 are the lifetimes of the fast and slow decay components, respectively. The fast component is generally attributed to non-radiative recombination through trap states, while the slower component corresponds to radiative recombination. The presence of both reflects second-order recombination processes. For samples deposited on transport layers, the decay curves required an additional term to account for carrier extraction or interfacial quenching. They were modelled with a triexponential fit, where the third component τ_3 captures recombination dynamics arising from interactions with the transport layer. Shorter lifetimes in this region can reflect efficient carrier extraction, while longer lifetimes may suggest poor interfacial contact or recombination losses. All TCSPC measurements were conducted using the Horiba DeltaFlex system (PPD-900 detector, Horiba Scientific), equipped with a 404 nm pulsed laser as the excitation source. Instrument settings such as laser power and integration time were kept constant for direct comparison across all samples.

Chapter 4: Enhancing reproducibility and phase stability in CsPbI₂Br photovoltaics through controlled processing

Summary

Addressing a persistent materials reproducibility challenge in CsPbI₂Br film formation; namely the consistent formation of the photoactive black α -phase rather than the non-active orange phase—this study begins by investigating how spin-coating time influences film quality and phase stability, gradually increasing the spin duration from 30 to 180 seconds to achieve more uniform films and improved α -phase formation after annealing. This prompted us to introduce a controlled pre-anneal hold step, where films were kept at room temperature for a short period before annealing at 160 °C, to further enhance reproducibility and phase purity. To understand the processes occurring during this step, we combined ATR-FTIR, *in situ* photoluminescence, and time-resolved X-ray diffraction to track solvent evaporation, intermediate phase formation, and crystallisation dynamics. These experiments revealed that crystallisation proceeds from the film surface downward, which motivated a systematic study of how varying hold duration affects microstructure, buried-interface quality, and defect formation. We then extended the investigation by reducing the pre-anneal temperature to suppress void growth and improve interface homogeneity, quantified using buried-interface SEM imaging and image-analysis workflows. Finally, we correlated these microstructural trends with photovoltaic performance, external quantum efficiency, and impedance spectroscopy, showing that optimised conditions, specifically a short hold at room temperature or a moderate hold at 15 °C, yield highly reproducible devices with low hysteresis, strong interfacial quality, and excellent long-term stability.

This study provides a comprehensive framework linking processing conditions to crystallisation pathways, void formation, and charge-carrier dynamics in CsPbI₂Br films. By demonstrating how careful control of spin-coating time, hold duration, and temperature leads to reproducible, high-quality perovskite absorbers, this work offers practical guidelines for improving the performance and operational stability of perovskite–silicon tandem solar cells.

4.1 Introduction

Metal halide perovskites (MHPs) have emerged as an attractive class of optoelectronic materials, gathering significant attention since their first application as active layers in photovoltaic (PV) devices nearly two decades ago.¹⁰ Their compositional tunability and the impact that facile elemental substitution has on their bandgap have enabled the development of a broad spectrum of hybrid organic–inorganic perovskites, advancing applications across photovoltaics (PVs), light-emitting diodes (LEDs), lasers, photodetectors (PDs), and other emerging technologies.^{113–118} In the PV space, they have accelerated the development of next-generation devices with remarkable improvements in power conversion efficiency (PCE) demonstrated over recent years, such that record certified PCE values now reached 18.49 %.¹⁷

Despite their outstanding optoelectronic properties, hybrid perovskites are fundamentally limited by their intrinsic instability under environmental exposure, such as moisture, light, and heat, leading to rapid degradation. As a result, interest has shifted towards all-inorganic perovskites as more stable alternatives, which offer enhanced thermal and photostability as well as better moisture resistance. Among the inorganic candidates, CsPbX_3 perovskites ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have emerged as highly promising materials due to their excellent thermal and environmental stability, tunable optoelectronic properties, and suitability for diverse applications ranging from photovoltaics to photonics. Bandgap tunability is exemplified by looking at halide substitution, progressing from CsPbCl_3 to CsPbBr_3 and CsPbI_3 , which results in a bandgap shift from 3.0 to 2.3 and 1.7 eV, respectively. This compositional flexibility allows further fine-tuning by preparing mixed-halide perovskites.

Of the mixed-halides, CsPbI_2Br has attracted particular attention because it combines the advantages of iodide- and bromide-based perovskites, balancing bandgap, phase stability, and environmental robustness. With a bandgap of ~ 1.92 eV, CsPbI_2Br is well suited as a top-cell material in perovskite–silicon tandem photovoltaics. However, reproducible fabrication of CsPbI_2Br films remains challenging due to issues with morphological non-uniformity, void formation at the buried interface, and uncontrolled phase transitions that can reduce device efficiency and stability^{119–121}. **Moreover, a recurring challenge in CsPbI_2Br processing is the inconsistent formation of the photoactive black α -phase, with films often transitioning to the non-active orange phase even under nominally identical fabrication conditions. This behaviour arises from the high sensitivity of CsPbI_2Br to subtle variations in the processing environment, including solvent evaporation rate, ambient conditions, precursor wet-film evolution, and thermal history during the pre-anneal and annealing stages. Small fluctuations in these parameters can alter the intermediate phase formation and crystallisation pathway, favouring the formation of the undesirable non-perovskite phase. As a result, achieving reliable α -phase formation requires careful control over the early-**

stage film evolution rather than relying solely on the final annealing step. Previous studies have proposed spin-coating methods to control crystallisation kinetics and improve film morphology, but systematic investigations into the combined effects of spin-coating duration, pre-anneal hold time, and hold temperature on film microstructure, buried-interface quality, and device performance remain limited¹²². Moreover, while hold steps are known to promote α -phase formation, their influence on void formation and charge-carrier dynamics has not been fully quantified.

In this study, we systematically investigate the influence of spin-coating time, pre-anneal hold duration, and hold temperature on the crystallisation dynamics, void formation, and optoelectronic properties of CsPbI₂Br films. Using time-resolved XRD, *in situ* photoluminescence, and buried-interface SEM analysis, we identify how solvent evaporation and intermediate-phase evolution govern top-down crystallisation and void growth. We further correlate these findings with photovoltaic performance metrics and impedance spectroscopy, as summarised in Table 1, which shows how prolonged hold times lead to increased void size, reduced XRD peak intensity, and longer non-radiative recombination lifetimes (t_2), indicating higher interfacial defect density. Devices fabricated under optimised conditions (RT 10 min and 15 °C 20 min) achieve PCEs around 12 % with low hysteresis, improved stability (>3000 h under N₂), and reduced series and bulk resistances, demonstrating the critical importance of controlling both hold time and temperature. This work therefore provides new insights into the coupled effects of processing parameters on buried-interface quality, enabling reproducible fabrication of high-performance CsPbI₂Br solar cells.

4.2 Influence of spin-coating duration (SC time)

Following the recent work of Byrannvand and co-authors¹²², the effect of spin-coating (SC) time on film quality and phase stability was studied. The SC time was increased from 30 to 180 seconds, resulting in more uniform films and improved α -phase formation after annealing, as shown in Figure 14a. This was confirmed by the X-ray diffraction (XRD) results in Figure 14b, where longer SC times were associated with stronger diffraction peaks, indicating better crystallinity. This improvement was observed even though film thickness decreased as SC time increased, as shown in Figure 14c. A reduction in secondary phases was also observed, as the shoulder on the (200) peak. Therefore, an SC duration of 180 s was used for the remainder of the study. However, challenges with reproducibility and uniform α -phase formation remained, especially when higher-concentration perovskite solutions were used, where secondary phases became more visible (Figure 14d). To address this, a hold step was introduced, where the films were kept at room temperature (RT)¹ for a few minutes before

¹ R.T. is taken to be the internal operating temperature of the glovebox *i.e.* 20-25 °C noting that there may be some day-to-day or seasonal variance. The controlled lower temperatures were achieved by a specialist cooling plate that ensured temperature control, accuracy and reproducibility. Following this work a temperature controller for the entire glovebox operation has been purchased and installed.

annealing at 160 °C (Figure 14e). Even a short 5-minute hold step consistently produced α -phase films for all solution concentrations and film thicknesses (Figure 14f).

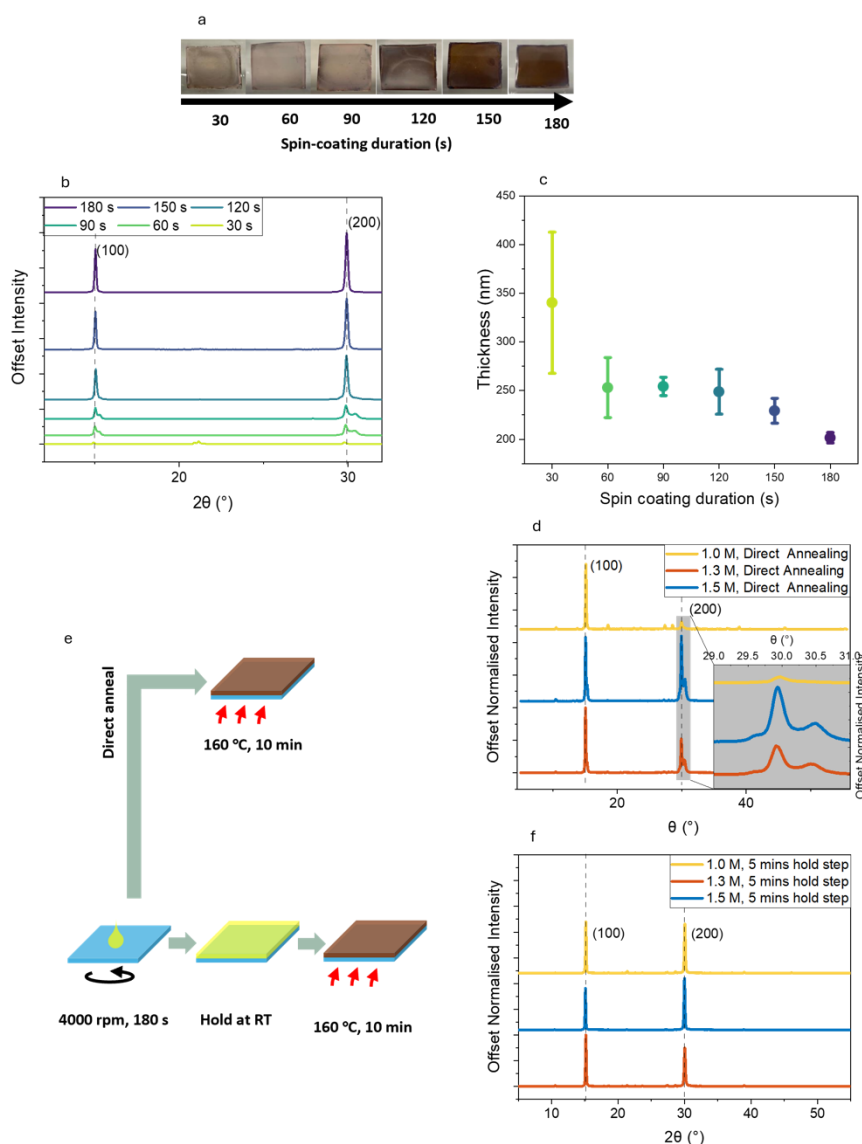


Figure 14 - Influence of spin-coating time and pre-anneal hold step on phase formation and film quality in CsPbI₂Br. (a) Photographs of films prepared with increasing spin-coating (SC) time from 30 to 180 s, showing improved visual uniformity and colour consistency. (b) XRD patterns of films prepared with different SC times, demonstrating increased diffraction intensity and reduced secondary phases with longer SC duration. (c) Measured film thickness as a function of SC time, showing a reduction in thickness despite improved crystallinity. (d) XRD patterns of films prepared from different precursor concentrations (1.0 M, 1.3 M, 1.5 M) under direct annealing, where higher concentrations exhibit increased secondary phases and reduced α -phase purity. (e) Schematic illustration of the introduced room-temperature hold step prior to annealing at 160 °C. (f) XRD patterns of films prepared from the same precursor concentrations after applying a 5-minute hold step, showing consistent formation of the α -phase and suppression of secondary phases across all thicknesses.

4.3 Role of pre-anneal hold duration in crystallisation

To investigate the processes occurring during the hold step, a series of measurements was carried out on the films under glovebox conditions (<0.1 ppm H_2O , <0.1 ppm O_2). Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was first performed on droplets of DMSO, DMF, and a 9:1 by volume mixture of DMSO:DMF (Figure 15a–c). By monitoring the change in absorption of key functional groups over time, a solvent evaporation behaviour was observed. As expected, pure DMF showed the fastest evaporation, followed by DMSO^{123,124}. However, much slower evaporation was observed for the 9:1 DMSO:DMF mixture compared to either solvent alone, which was attributed to molecular interactions between DMF and DMSO¹²⁵. ATR-FTIR was then performed on the same 9:1 mixture containing CsI, PbI_2 , and PbBr_2 in a 2:1:1 molar ratio (Figure 15d). The spectra were significantly different from those of the neat solvents, indicating that an intermediate phase was forming during the hold step. For example, the S=O stretch ($\sim 1044\text{ cm}^{-1}$) of DMSO showed a gradual intensity decrease, which was consistent with DMSO coordinating with lead halides to form complexes such as $\text{PbI}_2(\text{DMSO})_2$ or $\text{PbBr}_2(\text{DMSO})_2$ ¹²⁶. Similarly, the C=O stretch ($\sim 1670\text{ cm}^{-1}$) of DMF decreased in intensity due to solvent evaporation and the loss of its weaker coordination to lead halides¹²⁷. During the first 20 minutes, both the S=O and C=O absorption bands remained strong, indicating that solvent coordination with lead halide intermediates was maintained. Beyond this point, a gradual and progressive decrease in the intensity of both bands was observed, as solvent evaporation became the dominant factor. This interpretation is supported by the images taken of a film during the hold step after spin coating and before annealing (Figure 15d inset), where the films gradually changed colour from pale to yellow with increasing hold time, consistent with the formation of intermediate phases before crystallisation.

Following this, *in situ* photoluminescence (PL) measurements were performed on the perovskite films during the hold process to investigate the species formed during this time. The setup for these measurements, including the experimental design and hardware modifications, was developed during this PhD study, and complete specifications are provided in the experimental methods chapter. As shown in Figure 15e, no PL signal was detected during the early stages of the hold step ($t < 30$ minutes). However, emission peaks were observed beyond 30 minutes. A peak at 567 nm (2.19 eV) was first detected and was attributed to CsPbIBr_2 . At longer hold durations, a strong feature centred at ~ 810 nm appeared in the spectrum. This wavelength corresponds almost exactly to twice the excitation wavelength (405 nm) and is therefore attributed to a second-order diffraction artefact of the spectrometer rather than a genuine photoluminescence signal from the film. Such features are commonly observed in grating-based detection systems under short-wavelength excitation and do not represent a real electronic transition in the perovskite material.

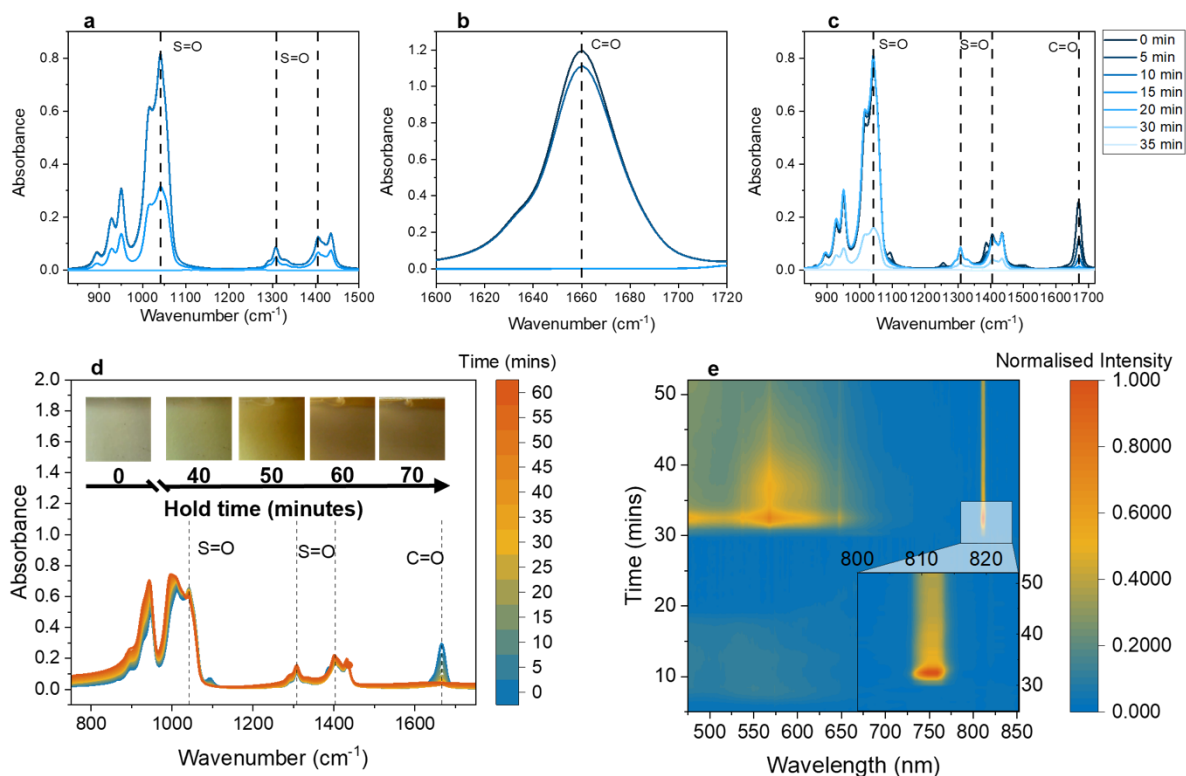


Figure 15- Characterisation of solvent evaporation, intermediate phase formation, and optical evolution during the pre-anneal hold step. (a) Time-resolved ATR-FTIR spectra of neat DMSO. (b) Time-resolved ATR-FTIR spectra of neat DMF. (c) Time-resolved ATR-FTIR spectra of a 9:1 DMSO:DMF mixture, showing slower evaporation compared to the neat solvents. (d) Time-resolved ATR-FTIR spectra of the 9:1 DMSO:DMF mixture containing CsI, PbI₂, and PbBr₂, demonstrating spectral changes associated with solvent coordination and intermediate phase formation; inset shows optical images of films during the hold step illustrating the gradual colour change with increasing hold time. (e) In-situ photoluminescence (PL) intensity map collected during the hold step, with inset highlighting the emergence of the emission band near ~810 nm at longer hold durations.

Additionally, structural changes taking place during the hold process were investigated using *in situ* X-ray diffraction (XRD). Conventional XRD measurements proved unsuitable for tracking these structural changes because commercially available sample holders and encapsulation approaches did not fully isolate the films from air during the highly sensitive hold stage. Several sealing strategies were tested but resulted in inconsistent phase observations due to residual air exposure. To overcome this limitation, a glovebox-integrated XRD system was employed and the measurement protocol was adapted to enable truly air-free, time-resolved structural characterisation during the hold process. To capture the structural evolution with finer time resolution, the scan range was narrowed to 28–31° 2θ and the scan duration reduced to 4 minutes, allowing more scans to be collected during the hold step (Figure 16a). This modification was only possible because the measurements were conducted inside the glovebox,

which allowed repeated rapid scans, ensuring that the observed phase evolution reflects intrinsic film behaviour rather than artefacts introduced by environmental exposure. From these data, three diffraction peaks were resolved over the scan range: one major peak at 29.5° 2θ and two smaller peaks at 29.8° 2θ and 30.6° 2θ . The relative changes in their peak positions, intensities, and full width at half maximum (FWHM) are shown in Figure 16b–e. The major peak (Peak 1) at 29.5° 2θ did not coincide with any diffraction peaks expected from bulk CsPbI_3 or CsPbI_2Br (Figure 16f). It was instead consistent with the formation of either a $\text{CsPbI}_x\text{Br}_{3-x}$ phase ($x > 2$) or 2D perovskites such as CsPb_2Br_5 or CsPb_2I_5 . The intensity of this peak increased slowly during the first 30 minutes of the hold and then more steadily over the following 50 minutes, suggesting a slow nucleation process followed by steady crystal growth, after which little change was observed (Figure 16b). The additional peaks (Peaks 2 and 3) could be assigned to the [200] reflections of CsPbI_2Br and CsPbIBr_2 , respectively. Peak 2 exhibited a gradual increase in intensity, starting around 40 minutes, and plateaued near 70 minutes, whereas Peak 3 showed no significant change in intensity. The FWHM of all three peaks was also extracted from the time-resolved data (Figure 16d). Since peak broadening may coincide with changes in intensity, the effective FWHM (integral breadth) was also calculated as a more robust indicator of peak broadening. Both analyses showed similar trends: an initial decrease in FWHM during the first 20 minutes, a plateau between 40–50 minutes, and a gradual increase until approximately 120 minutes of total hold time. This initial narrowing can be attributed to an increase in grain size with longer hold durations^{128–131}, whereas the later broadening is consistent with reduced coherent domain size and/or increased microstrain. A comparison between films that were held for 150 minutes then annealed and films that were not annealed (Figure 16e) showed clear differences. In the annealed film, only Peak 2 remained, suggesting that the low-temperature crystallisation observed during the room-temperature hold was driven by solvent evaporation from the surface, leading to surface-to-bulk crystallisation, which was followed by a thermally induced phase transformation to the more stable CsPbI_2Br phase during annealing. Figure 16e, also shows the XRD data for a film held for 40 minutes and then annealed at 160°C . In the non-annealed film, Peak 1 from the time-resolved data and its lower-order reflection near 14.7° 2θ were clearly present. After annealing, both peaks shifted slightly to higher 2θ values, aligning with the (100) and (200) peaks of CsPbI_2Br . These peaks also increased significantly in intensity and showed a reduction in FWHM, indicating improved crystal quality and phase purity. Finally, reference films of CsPbI_3 , CsPbI_2Br , and CsPbIBr_2 were prepared using conventional routes and their diffraction patterns collected over the same $28\text{--}32^\circ$ 2θ range (Figure 16f). These data confirmed the formation of phase-pure 3D CsPbI_2Br and the absence of other phases.

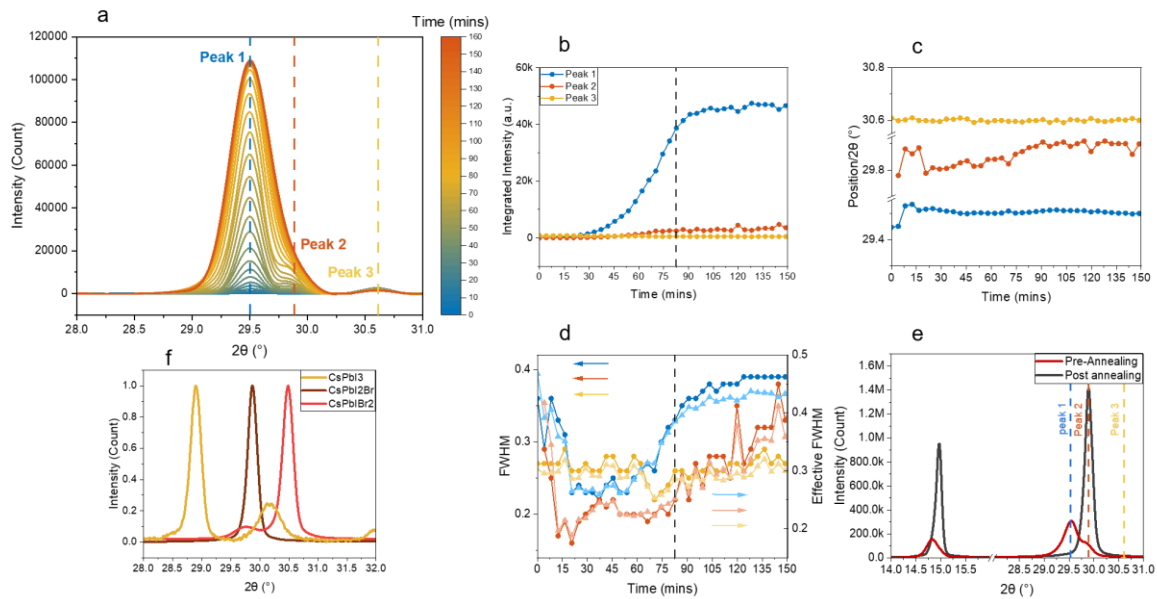


Figure 16 - Time-resolved XRD during the room-temperature hold step and subsequent annealing. (a) Stacked XRD scans collected every 4 minutes in a narrowed 28–31° 2θ window, enabling faster measurements and improved time resolution to follow structural evolution during the hold step; Peaks 1–3 are marked. (b) Integrated intensities of the three peaks as a function of hold time. (c) Evolution of peak positions with hold time. (d) FWHM and corresponding integral breadth versus hold time. (e) XRD comparison of films held for 150 minutes at room temperature with and without subsequent annealing at 160 °C, as indicated by the legend. (f) Reference diffraction patterns of CsPbI₃, CsPbI₂Br, and CsPbIBr₂ shown over the same 28–32° 2θ range for phase identification.

While holding the films before annealing affects the final phase purity, the effect of the hold duration still needed to be understood. Films were held for 0, 10, 20, 30, and 40 minutes at RT and then annealed at 160 °C. We observed a viewing-direction effect: when viewed from the top the films looked uniform in colour, but when viewed from the back, the films appeared hazy, and this haze became stronger as the hold time increased (Figure 17a). This behaviour is linked to a poor, inhomogeneous buried interface, which is known to harm photovoltaic performance¹³². Such voids are consistent with crystallisation that starts at the top surface and grows down through the film, trapping solvent at the buried interface that later leaves voids during annealing (Figure 17b)^{99,133}. Even so, the absorption onsets and the derived band gaps were similar across the series (Figure 17c), indicating compositional homogeneity. The XRD data in Figure 17d show that the observed non-uniform appearance is not due to unwanted phases; instead, the hold time mainly affects film formation and microstructure rather than the final crystal phase. A drop in XRD peak intensity with longer pre-anneal holds was observed, which can be explained by a lower effective diffracting volume and extra scattering from interfacial voids created during slower, top-down crystallisation, rather than a change in composition or phase. It is also noted that films processed without a hold (0 minutes) can

show the longest absorption cut-off and, in some cases, form a photo-inactive orange film instead of the black photoactive film. By contrast, introducing a hold step before thermal annealing consistently **always** photoactive CsPbI_2Br .

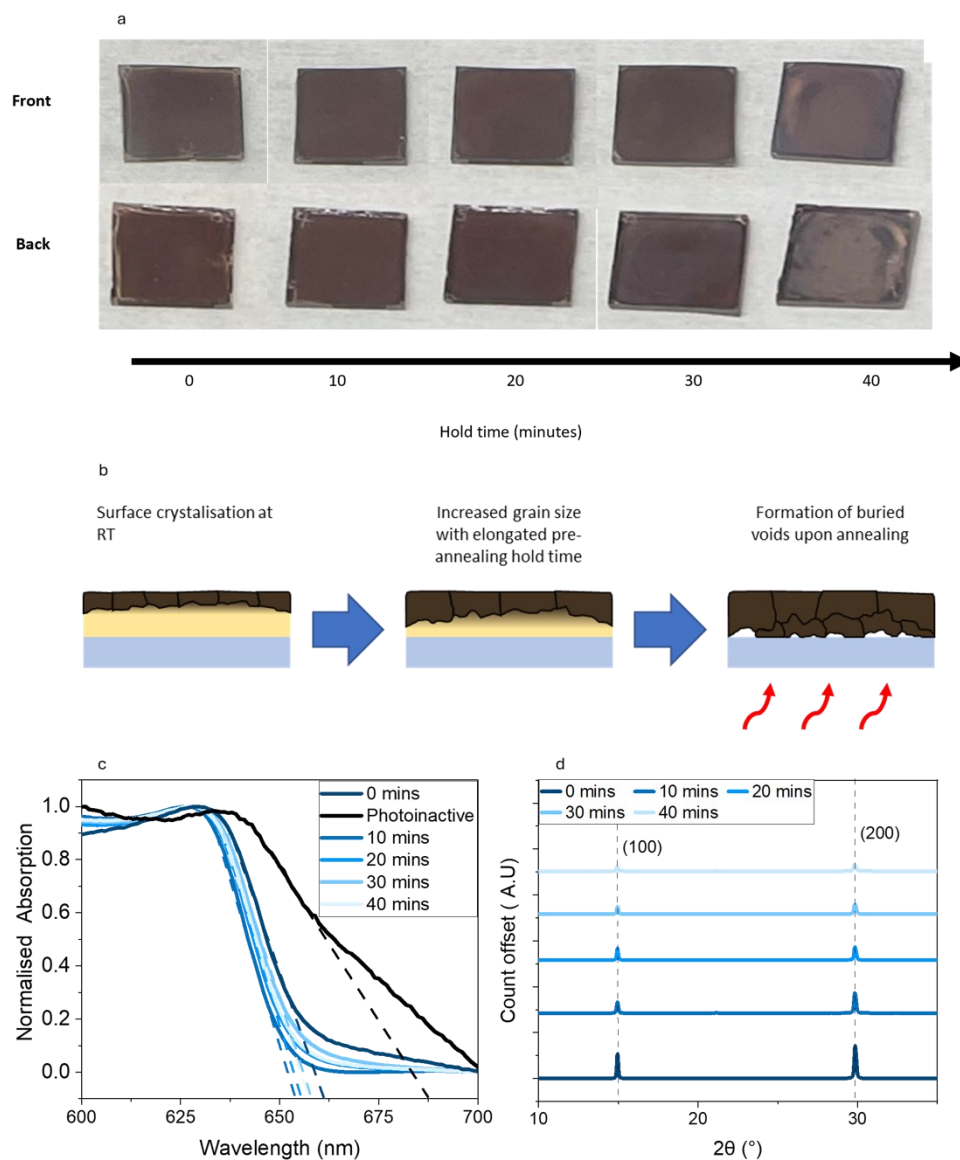


Figure 17 - Effect of room-temperature hold duration before annealing on film formation and buried-interface quality. (a) Photographs of films held for 0, 10, 20, 30, and 40 minutes, shown from the top and from the back; increased haze from the back with longer hold times indicates changes at the buried interface (Substrate is 12x12 mm²). (b) Schematic illustration of top-down crystallisation during the hold step, leading to solvent entrapment and void formation at the buried interface upon annealing. (c) Absorption spectra and corresponding band gaps for films held for different durations, showing similar absorption onsets and compositional homogeneity in films other than the photoinactive film. (d) XRD patterns after annealing at 160 °C for films held 0–40 minutes, demonstrating that changes in appearance arise from microstructural differences rather than phase changes.

To further confirm the impact of reduced buried interface quality on overall film performance, light intensity-dependent time-correlated single-photon counting (TCSPC) measurements were conducted to reveal how different recombination pathways compete and change with excitation density. TCSPC was performed on films deposited on bare glass and SnO₂-coated glass with pre-annealing hold times ranging from 10 to 40 minutes. The data for the bare glass samples were fitted using a bi-exponential decay model, while those on SnO₂ were fitted with a tri-exponential model, as summarised in Table 1. According to Yuan *et. al.* ¹³⁴, the longest lifetime corresponds to radiative recombination, the second longest to non-radiative recombination, and the shortest to ETL interaction. This is consistent with Sidhiket. *al.* ¹³⁵, who report that t_1 (fastest) and t_2 (fast) are associated with non-radiative recombination, whereas t_3 (slowest) reflects radiative recombination.

As shown in Table 1, longer hold times, specially 40 minutes, result in extended t_2 in the back-side measurements of the glass samples (e.g., 52.38 ns at 40 minutes). Longer lifetime elements, t_2 , are associated with radiative recombination, and looking at its relative contributions of A_2 , we observe it increases with the increase of the pre-hold time. It goes from 0.24 in the samples 10 and 20 mins to 0.5 in the 40 mins sample where it significantly increases. This indicates that prolonged hold times results in better quality at the back side of the films despite the increase in voids. Front-side measurements show relatively shorter and more consistent t_2 values across hold times from 20 to 40 mins (e.g., 32.86 ns at 40 min vs 30.49 ns at 20 min). The shortest hold time (10 min) shows significantly longer t_2 for front-side excitation of 58.10 ns. The A_2 trend in front side is similar to that at the back side. As for the shorter lifetime t_1 , it is associated with non-radiative recombination. We observe a drop in relative contributions, A_1 , of non-radiative recombination with the increased per-hold time on both the front and back, suggesting reduced nonradiative recombination with increased per-annelaing hold time likely due to enhanced film quality. For the SnO₂-coated samples, the fastist lifetime t_1 corresponds to non-radiative recombination, and the slightly slower lifetime, t_2 , corresponds to interfacialy non-radiative recombination due to the introduction of the transport layer. Table 1 shows consistently lower radiative recombination lifetime compared to the glass samples which reflects a quenching effect due to the charge extraction. Across samples, the increased hold time increases the lifetime of radiative recombination on both sides, especially at the back side. This reflects the enhanced film quality as a result of increased hols time. These results highlight the defects passivation effect of SnO₂, which suppresses non-radiative pathways Across samples, increased hold time reduces the non-radiative recombination at the back side but increases it at the front, which possibly confirming the passivation effect at the back side. As for the interfacial non-radiative element we observe that it icreases with the increase of the epr annealing hold time at the back side measurement. This is likely due to the increased back voids resulting in lower contact area and hindered charge extractions. Overall, these findings demonstrate that optimising pre-annealing hold time is critical for reducing interface defect density.

Table 1 - The TCSPC parameters summary of films fabricated with different pre-annealing times, measured on glass substrates. F is for front and B is for back

	40 min		30 min		20 min		10 min	
	F	B	F	B	F	B	F	B
Glass								
A ₁	0.40	0.35	0.53	0.60	0.68	0.79	0.72	0.76
t ₁ (ns)	1.23	1.54	1.44	0.71	0.69	0.49	0.72	0.51
A ₂	0.47	0.50	0.29	0.30	0.20	0.24	0.18	0.24
t ₂ (ns)	32.86	52.38	34.29	34.58	30.49	40.37	58.10	48.60
t _{average} (ns)	31.89	51.37	31.96	33.25	28.41	38.83	55.33	47.09
SnO ₂								
A ₁	0.89	0.28	0.76	0.31	0.66	0.66	0.57	0.60
t ₁ (ns)	0.33	1.62	0.22	1.28	0.26	0.21	0.30	0.20
A ₂	0.25	0.92	0.40	0.88	0.35	0.37	0.49	0.43
t ₂ (ns)	1.91	0.21	1.36	0.23	2.64	2.01	2.03	1.52
A ₃	0.05	0.04	0.05	0.04	0.16	0.16	0.07	0.15
t ₃ (ns)	14.76	13.01	7.14	9.10	10.03	7.88	10.46	4.93
T _{average} (ns)	1.27	0.95	0.91	0.76	2.34	1.81	1.65	1.29

4.4 Quantifying buried-interface voids versus pre-anneal hold time and temperature

To study the impact of hold duration and temperature on the films formed, scanning electron microscopy (SEM) of the buried interface was carried out (Figure 18 and Figure A 1 in appendix II). It was immediately apparent that the average grain size increased as the hold time increased and as the temperature was reduced (Figure 18). This trend is consistent with slower nucleation and crystallisation during the pre-anneal step^{130,136} Taken together, the observations suggest that pre-annealing allows intermediate phases to form fully and promotes a more controlled crystallisation, giving larger grains, which can benefit device performance by reducing the number of grain boundaries.

From the large image set collected, a simple image-processing workflow was developed to quantify the density and size distribution of voids at the buried interface. Full details are provided in the Experimental Methods chapter. Briefly, 15 SEM images per condition were analysed; voids were segmented, and both total void area and the size distribution were extracted. For each image, the void area was normalised to the imaged area and treated as a single data point. Each image covers $128.34\ \mu\text{m}^2$, ensuring consistent sampling across all conditions. Representative segmented images used for the void analysis are shown in Figure 18 and Figure A 1 in the Appendix II. Voids are present even when no pre-anneal is used, showing that pre-annealing alone does not introduce interfacial defects and that processing temperature is also important. For samples prepared at RT, the void size increases with hold time and the size distribution broadens; by 40 minutes, the number of voids is low because a few large voids dominate. This behaviour is consistent with coalescence of nearby voids, analogous to an Ostwald-type ripening process.

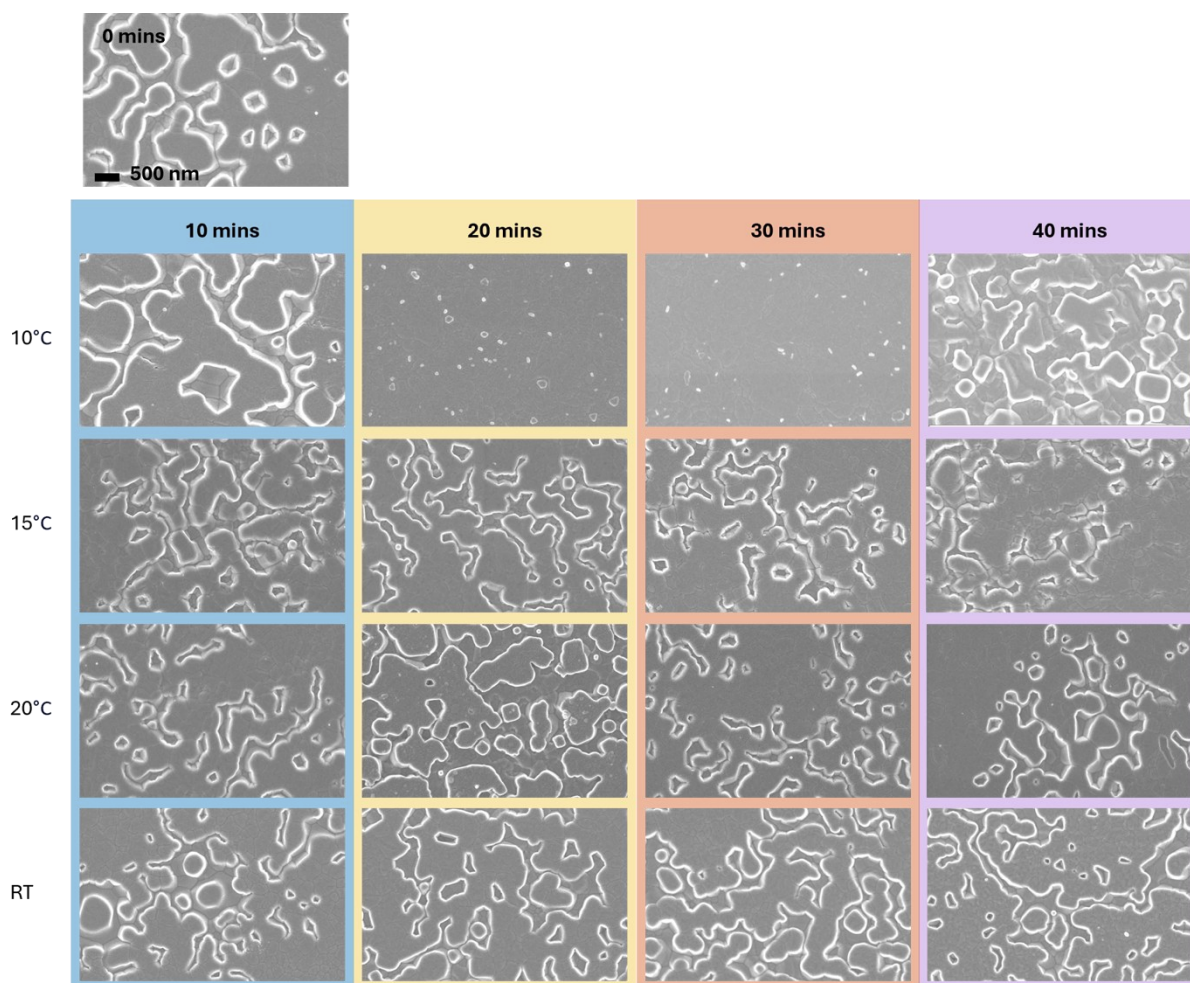


Figure 18 - Buried-interface SEM images as a function of hold duration and hold temperature. A reference micrograph for 0 min hold is shown at the top left. Columns correspond to films held for 10, 20, 30, and 40 minutes prior to annealing, while rows correspond to different temperatures used during the hold step. All images are taken at the same magnification and scale, enabling direct comparison of void size and distribution at the buried interface. These images were used for the void segmentation and quantitative analysis described in the text. Scale bar: 500 nm.

The box plot analysis (Figure 19a) quantifies these observations, showing significantly larger void-to-film ratios in samples prepared without temperature control (RT). The variability in these samples is evident from the wider interquartile ranges and extended whiskers, reflecting the substantial heterogeneity in void size distribution under these conditions. In contrast, reducing the pre-annealing temperature to below 20 °C leads to a marked decrease in void density across most samples, except for the shortest hold time at 20 °C. This indicates that controlling the pre-annealing temperature is an effective strategy to manage void formation. Since the glovebox typically operates close to 20 °C, it is unsurprising that the data for 20 °C samples closely match those of the uncontrolled RT samples. As the pre-annealing time increases, there is a gradual broadening of the distribution and a shift towards larger void sizes, as seen in the box plots. This spread, while still present, is less pronounced

at lower temperatures compared to RT, suggesting that lower temperatures slow down void growth. At 15 °C, void counts are generally lower and more consistent than at RT, as indicated by the narrower spread in the box plots. This suggests that cooler preparation temperatures help suppress void formation during fabrication, consistent with the results reported by Matsuda *et. al.*¹³⁷, who found that spin-coating below 20 °C yields pinhole-free, dense grain structures, while higher temperatures lead to voids and reduced film coverage. It is also worth noting that the total void areas reported for 15 °C samples are comparable to those prepared with a pre-annealing step. When the temperature is further reduced to 10 °C, similar behaviour to that observed at 15 °C and 20 °C is seen, but with greater variability, as shown by the broader data spread in Figure 19a. Despite careful image segmentation, sample cracking between void regions may not have been fully accounted for, possibly affecting the results (Figure 19b–c). This behaviour can be explained by considering the thermal stress induced when the sample transitions from cooling to the 160 °C hotplate; thus, 10 °C likely represents the lower limit of effective cooling treatment. The glass substrates showed no signs of thermal shock during this process.

The void size distributions (Figure 19d–g) reveal that in all conditions, void sizes are predominantly clustered at the lower end of the scale, confirming that small voids are more common while large voids are relatively rare. In the RT samples, shorter hold times show a higher frequency of smaller voids, while longer hold times shift the distribution towards larger void sizes. In contrast, the 10 °C samples show no clear correlation between hold time and void size. Interestingly, shorter hold times (10–20 min) in the 10 °C samples exhibit a larger number of voids than the longer hold times (20–30 min), which may be attributed to cracking effects introducing significant error. The samples fabricated at 15 °C and 10 °C show very similar void size distributions, suggesting a more uniform interface and improved film quality.

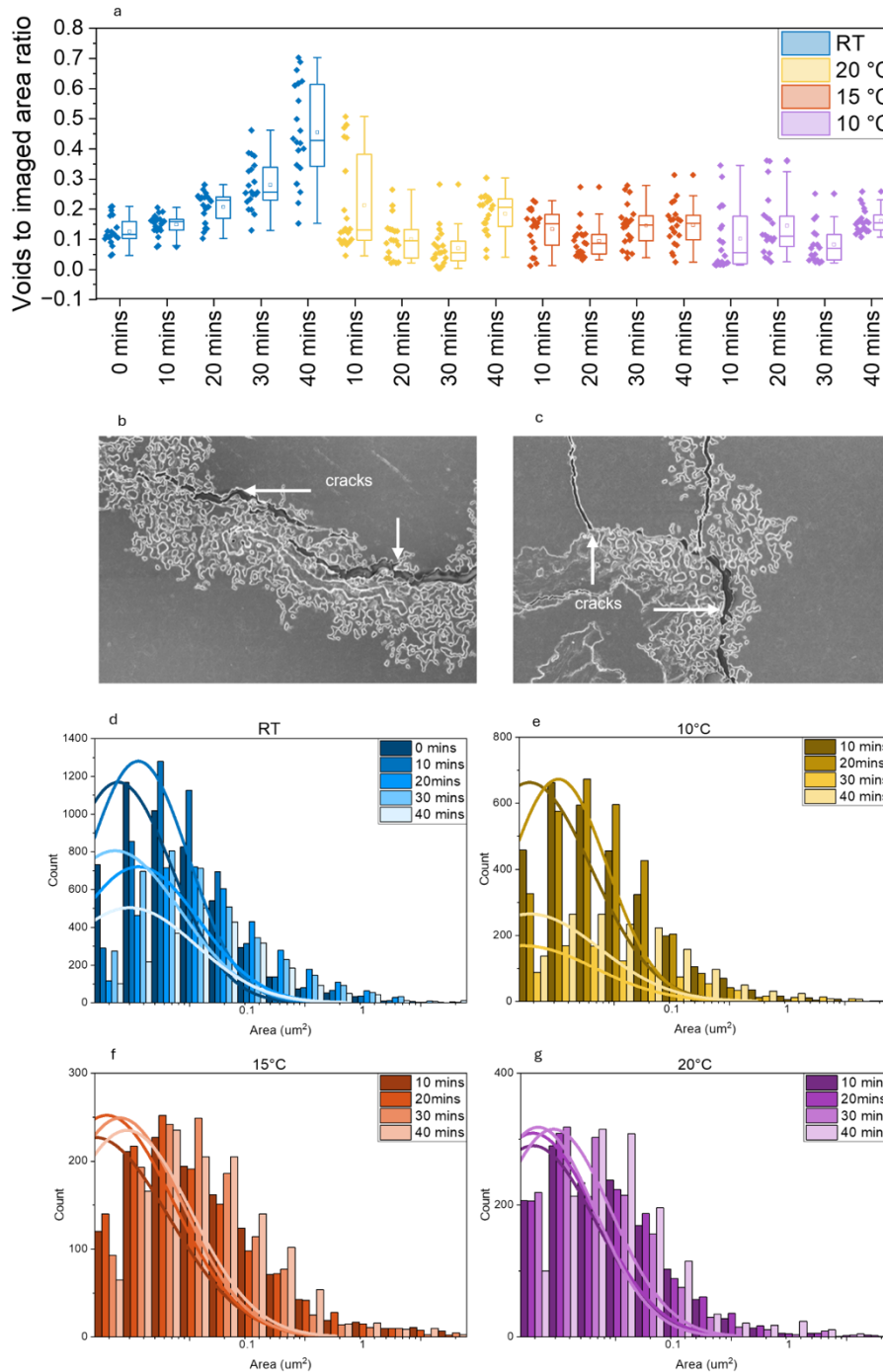


Figure 19 - Quantification of buried-interface voids as a function of hold temperature and duration. (a) Box plots of void-to-film area fraction extracted from segmented SEM images for samples prepared at RT, 20 °C, 15 °C, and 10 °C across different hold times; boxes represent interquartile range with whiskers showing data spread. (b–c) Representative segmented SEM images from 10 °C samples highlighting cracking between void regions that can influence void quantification. (d–g) Log-scale void-size distributions for RT, 20 °C, 15 °C, and 10 °C, respectively, showing the frequency of void sizes with fitted trend curves to illustrate distribution behaviour. Colours correspond to different hold durations as indicated in the legends.

4.5 Impact of pre-anneal processing on device performance

To understand the impact of the pre-annealing step on device performance, photovoltaic cells were fabricated using perovskite absorber layers exposed to pre-annealing temperatures of 15 °C and RT for various hold durations. The solar cells used the same architecture described in the Experimental section: ITO/MeO-2PACz/CsPnI₂Br/C₆₀/BCP/Ag. Device characterisation was performed following the procedures detailed in the Experimental Methods section.

The key performance metrics, namely power conversion efficiency (PCE), open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF), for all devices are summarised in the box plots shown in Figure 20a–d. From these plots, it is clear that the devices prepared at RT with a 10-minute hold and those prepared at 15 °C with a 20-minute hold achieved the highest PCEs, both around 12 %. These two conditions also exhibit the smallest spread in PCE, V_{oc} and FF, indicating excellent reproducibility. By contrast, devices prepared with longer hold times (30 and 40 min) exhibited a noticeable reduction in performance, characterised by lower PCE values that correlate with the increased void formation reported in Figure 19. Notably, RT devices held for 30 and 40 min were completely non-functional, as seen from the zero PCE data points. V_{oc} follows a similar trend for the RT samples, with the 10 min devices giving the most consistent values, while the 20 min devices show a significantly larger spread, suggesting variability in interface quality. At 15 °C, V_{oc} values remain relatively consistent across hold times (approximately 1.05–1.15 V), with the 15 °C, 20 min devices slightly outperforming the RT 10 min devices. J_{sc} shows more variation across all conditions. RT 10 min and 20 min devices exhibit relatively similar J_{sc} values, while the 15 °C devices display a clear trend: the mean J_{sc} gradually decreases with longer hold times, and the spread becomes narrower, indicating more uniform but slightly reduced photocurrent generation. This behaviour is consistent with hindered charge extraction caused by the increased void density at longer hold times. Interestingly, FF appears to increase as the median void area increases, showing an opposite trend to J_{sc} . This could be because a larger void area reduces the physical contact area between the perovskite layer and the bottom HTL (MeO-2PACz), which might reduce interfacial recombination losses and increase series resistance.

Wang *et al.* demonstrated that voids play a critical role in reducing thermal and light stability, exacerbating recombination losses and contributing to device degradation over time⁹⁹. These findings are consistent with the stability data in Figure 20e–f, where devices fabricated under the optimal conditions (RT 10 min and 15 °C 20 min) maintained stable PCE, V_{oc} , J_{sc} and FF under N₂ storage for over 3000 hours. Unlike the high-void-density devices, which exhibited accelerated degradation and phase instability (Figure 20f), these optimised devices preserved the photoactive black phase,

supporting the link between reduced void density, improved interface quality and enhanced operational stability.

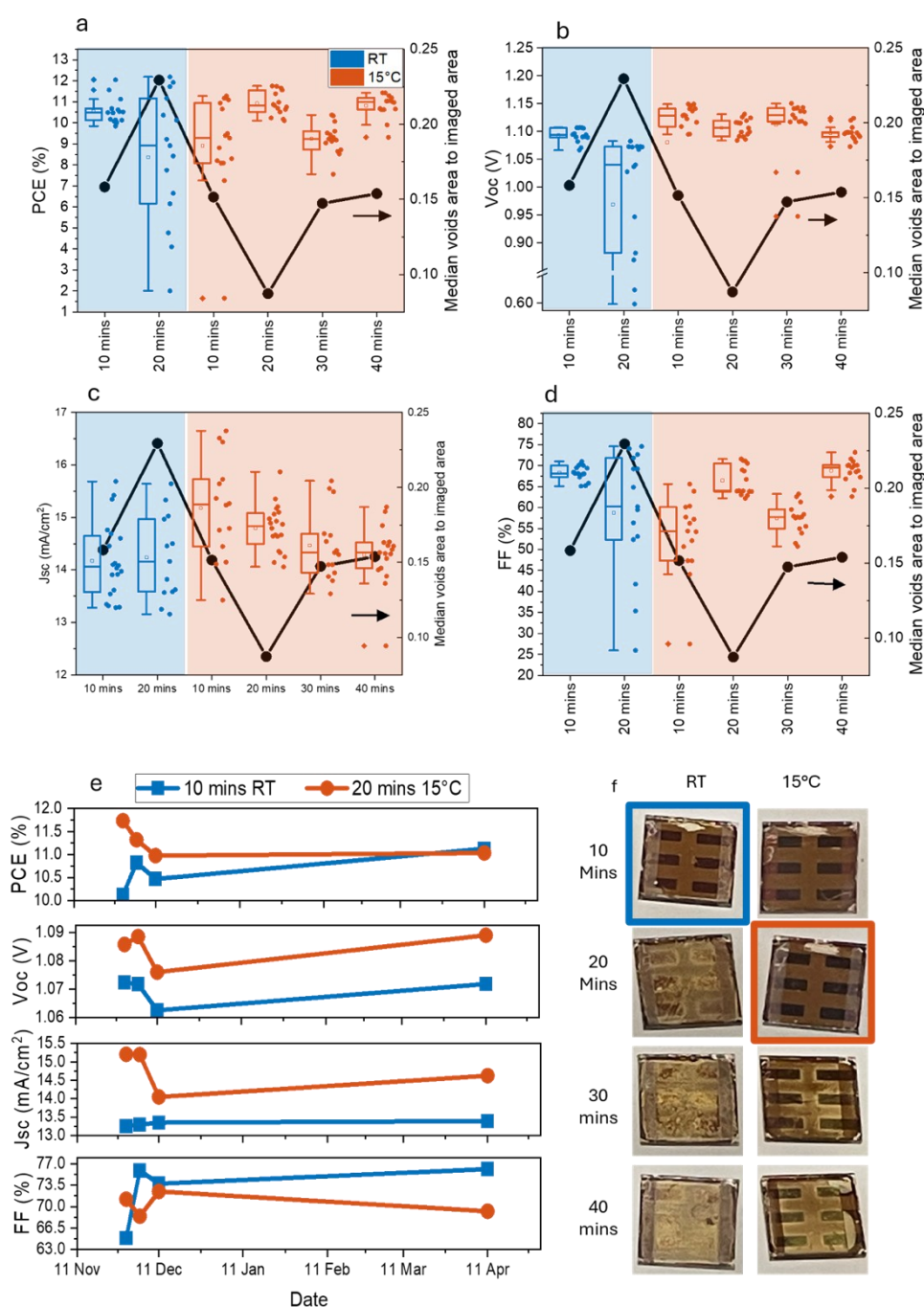


Figure 20 - Device performance and long-term stability as a function of pre-anneal hold duration and temperature. (a–d) Box plots of Jsc, Voc, FF, and PCE for devices fabricated with hold times of 0–40 minutes at RT (blue) and 15 °C (orange). (e) Evolution of Jsc, Voc, FF, and PCE over 3000 hours for representative devices stored under N₂, corresponding to the optimal processing conditions identified in (a–d). (f) Photographs of the back side of the same devices after ageing, illustrating visual degradation trends associated with increased void formation.

The forward and reverse J–V scans for the champion devices prepared at RT and 15 °C are shown in Figure 21a. These curves demonstrate excellent diode behaviour with steep rectification and minimal hysteresis between forward and reverse scans, indicating well-formed junctions, high-quality interfaces, and minimal trap-assisted recombination losses. These characteristics are consistent with reduced void formation and improved interfacial integrity, as also suggested by the morphological analysis (Figure 18 and Figure 19). The corresponding external quantum efficiency (EQE) spectra for the champion devices are presented in Figure 21b. Both devices exhibit strong photocurrent generation across the visible spectrum, with high EQE values between 400–750 nm, and the integrated J_{sc} values closely match those obtained from the J–V scans. This close agreement confirms that the measured device photocurrents are reliable and not significantly influenced by hysteresis or light soaking effects. The relatively flat EQE response across the visible range indicates efficient light absorption and minimal parasitic optical losses, while the well-matched integrated J_{sc} values underscore effective charge extraction in both RT and 15 °C devices. Interestingly, the overall performance of the RT and 15 °C champion devices is very similar, despite the differences in pre-annealing temperature. This can be attributed to the comparable total thermal budget (combined hold and anneal times) in both cases, which likely resulted in similar crystallisation dynamics and interface formation. Nevertheless, SEM imaging revealed the presence of voids at the buried interface under some conditions, which are known to act as recombination centres and can lower V_{oc} , J_{sc} , and overall PCE. These observations highlight the need to minimise void density and optimise interfacial properties through careful control of both temperature and hold time. Reducing the pre-annealing temperature improves void suppression, while selecting an appropriate hold time enhances crystallinity and interface uniformity, balancing these factors is critical to maximising device efficiency. These findings align with reports by Zeng *et al.*, who demonstrated that eliminating buried interfacial voids significantly enhances PCE by improving charge extraction and minimising recombination losses ⁹⁵. Similarly, Wang *et al.* reported that voids in perovskite films near the buried interface contribute to increased non-radiative recombination and degradation in stability, underscoring the necessity of optimising processing conditions to suppress void formation ⁹⁹.

4.6 Pre-anneal conditions impact on defect density and charge transport

Impedance spectra were collected for the same samples and fitted with an $R||RC||RC$ equivalent circuit (77c) at 1 V, providing critical insights into the electrical properties of the champion devices prepared at RT for 10 minutes and 15 °C for 20 minutes. The Nyquist plot (Figure 21d) shows a smaller semicircle for the 15 °C 20-minute device, indicating lower overall impedance compared to the RT 10-minute device, which exhibits a larger semicircle reflecting higher charge transfer resistance and recombination losses. The extracted series resistance (R_{series}) for the 15 °C 20-minute

device is lower (39.68 Ω) than that of RT 10 minutes (70.95 Ω), suggesting improved contact resistance. Similarly, the recombination resistance ($R_{\text{recombination}}$) at the interface is significantly higher for the 15 °C 20-minute sample (247.9 Ω) compared to RT 10 minutes (~ 0 Ω), indicating suppressed interfacial recombination due to reduced void formation and improved interface quality. The bulk resistance (R_{Bulk}), associated with the perovskite layer, is lower for the 15 °C 20-minute device (83.6 Ω vs. 308.4 Ω), reflecting enhanced charge transport and reduced bulk defect density. The phase plot (Figure 21e) shows a sharper dip at higher frequencies for the 15 °C 20-minute device. Moreover, the capacitance values ($C_{\text{recombination}}$ and C_{Bulk}) for the 15 °C 20-minute device suggest better charge storage and extraction, further supporting its improved performance. The modulus plot (Figure 21f) shows lower impedance across all frequencies for the 15 °C 20-minute device, confirming reduced defect-related charge trapping.

The capacitance (C) and depletion width (W) trends further highlight differences in junction quality. The higher capacitance for the 15 °C 20-minute device corresponds to a narrower depletion width ($W = \epsilon\epsilon_0 A/C$), which allows faster charge extraction and reduces charge trapping¹³⁸. Meanwhile, the lower capacitance of the RT 10-minute device results in a wider depletion width, slowing charge separation and increasing recombination losses. The smaller W and stronger electric field in the 15 °C 20-minute device ensure superior charge collection efficiency, aligning with its higher J_{sc} and fill factor (FF) compared to the RT 10-minute sample.

Figure 21g provides additional evidence linking device performance to morphology. The 15 °C 20-minute device shows a higher V_{oc} under illumination compared to the RT 10-minute device, which correlates with the higher J_{sc} and FF values reported in the table. The ideality factor, extracted from V_{oc} versus illumination intensity, is lower for the 15 °C 20-minute device, approaching ideal diode behaviour ($n \approx 1$) and confirming suppression of trap-assisted recombination pathways. The median void area is also significantly smaller for the 15 °C 20-minute device, indicating improved perovskite coverage and fewer shunting paths Figure 21h. These findings align with the lower R_{Bulk} and R_{series} , and higher $R_{\text{recombination}}$ values obtained from the EIS fitting (Figure 21f), all indicating reduced defect density and improved interface quality. Together, the higher V_{oc} , lower ideality factor, and smaller void area explain the superior FF and overall PCE of the 15 °C 20-minute device compared to the RT 10-minute device.

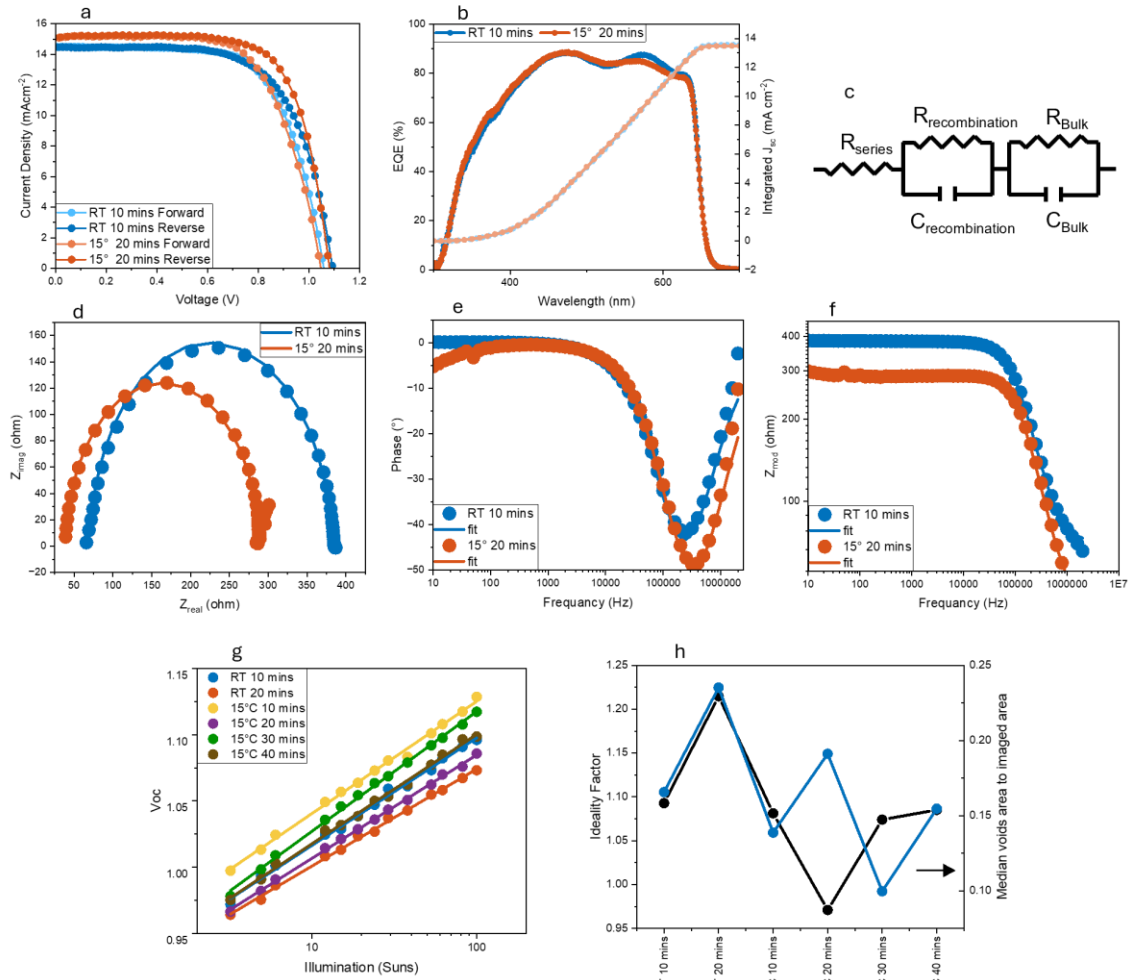


Figure 21 - Electrical characterisation of champion devices prepared under the optimal pre-anneal conditions identified in Figure 20: RT for 10 minutes (blue) and 15 °C for 20 minutes (orange). (a) Forward and reverse J–V characteristics under illumination. (b) External quantum efficiency (EQE) spectra with integrated J_{sc} . (c) Equivalent circuit used to fit the impedance spectroscopy data ($R||RC||RC$). (d) Nyquist plot from impedance spectroscopy showing the fitted response. (e) Bode phase plot derived from the same EIS measurements. (f) Bode magnitude plot ($|Z|$) as a function of frequency. (g) Open-circuit voltage (V_{oc}) as a function of illumination intensity for extraction of the ideality factor. (h) Comparison of extracted ideality factor and median void area, linking electrical behaviour to buried-interface morphology.

4.7 Closing remarks

In this chapter, we have demonstrated how careful control of spin-coating time, pre-anneal hold duration, and temperature enables precise control over crystallisation dynamics, void formation, and interface quality in CsPbI_2Br films. Through a combination of *in situ* characterisation techniques and systematic optimisation, we established clear links between processing parameters, buried-interface

morphology, and final device performance. Importantly, we showed that a short room-temperature hold or a moderate hold at 15 °C reliably produces phase-pure, uniform films with reduced void density and improved interfacial contact. When integrated into photovoltaic devices, these optimised films delivered highly reproducible performance, minimal hysteresis, and excellent operational stability under inert storage.

These findings highlight the critical role of pre-anneal processing in determining the quality and reliability of all-inorganic perovskite absorbers. The methodology presented here provides a practical framework for fabricating high-performance, stable CsPbI₂Br solar cells and offers valuable insights for scaling up perovskite–silicon tandem technologies. Future work could extend this approach to other mixed-halide systems and explore automated process control for even greater reproducibility in large-area devices.

Chapter 5: Warm-air-assisted, slow-cooling Ambient Processing Reveals Oxygen-Driven Intense Photoluminescence and Stability in CsPb(I,Br)₃ Films

Summary

All-inorganic CsPbI₂Br perovskites are attractive candidates for stable, wide-bandgap (E_g) photovoltaics and tandem solar cells, but fabricating high-quality films under ambient conditions remains challenging. Ambient processing often forces a trade-off between film uniformity, photoluminescence, phase stability, and interfacial energetics, limiting reproducibility and device performance. In this work, a reproducible fabrication strategy was developed that combines solvent engineering, controlled warm-air exposure, a two-step deposition process, and a slow post-annealing cool-down to overcome these limitations. Structural, morphological, and optical characterisation using SEM, UV-Vis, PL, XRD, and GIXRD confirmed that this approach produces uniform, pinhole-free, and phase-pure films with improved crystallographic quality. Surface and electronic characterisation (APS, KP, XPS, ARXPS) revealed that slow cooling promotes oxygen incorporation, shifts the band edges towards the vacuum level, and induces p-type doping. Urbach energy analysis, steady-state and intensity-dependent PL, and TCSPC measurements showed reduced energetic disorder, suppressed non-radiative losses, and a higher fraction of radiative recombination. *In-situ* UV-Vis and PL stability tests demonstrated that the slowly cooled films retain the photoactive α -phase and maintain strong emission under extended air exposure, in contrast to the rapid degradation observed in rapidly cooled films. Finally, photovoltaic devices were fabricated under all processing conditions and evaluated by J-V analysis, EQE, TPV/TPC, and EIS. These measurements revealed that, although slow cooling enhances optical quality and stability, device performance remains governed by interfacial energetics and charge-extraction barriers rather than bulk film quality.

5.1 Introduction

All-inorganic halide perovskite materials, particularly CsPbI_2Br , have emerged as promising candidates for photovoltaic (PV) applications owing to their thermal stability and suitable bandgap for silicon-tandem integration ⁸⁷. Compared to organic-inorganic hybrid perovskites, CsPbI_2Br exhibits enhanced resistance to phase degradation under elevated temperature and humidity, making it attractive for practical deployment. However, achieving high-quality CsPbI_2Br films under ambient conditions remains a challenge with approaches being reliant on glovebox processing and toxic antisolvents ¹³⁹. Recent advances have sought to overcome these limitations through hot-air-assisted and fully air-processed approaches. Dynamic hot-air-assisted deposition has proven effective in controlling solvent evaporation kinetics, thereby promoting intermediate-phase formation and yielding dense, uniform films ⁸². Barium incorporation via this strategy further enhances stability of the photoactive α -phase and suppresses non-radiative recombination. This enables devices with power conversion efficiencies (PCEs) > 14 % and good operational stability under ambient conditions ¹⁴⁰. Extensions of this approach with alternative dopants, including europium and indium, have resulted in single-junction devices with PCEs up to 17 % while maintaining reproducibility and long-term durability ¹⁴⁰. Beyond hot-air processing, solvent and additive engineering approaches have been introduced to improve CsPbI_2Br -based devices. The use of DMSO as a co-solvent is commonly used to slow crystallisation, whilst thiourea additives passivate defects and direct grain growth, producing uniform, pinhole-free films and PCEs > 7 % ¹⁴¹. Hot-substrate deposition methods have also been explored, where pre-heating promotes rapid solvent evaporation and nucleation, enabling large-grain CsPbI_2Br films with PCEs > 9 % while avoiding high-temperature annealing ⁸³. Crystallisation management strategies, including interface engineering with NaF-modified SnO_2 , have further demonstrated record fill factors, > 84 %, and PCEs > 17 % ¹⁴².

Despite these advances, there remain gaps in understanding of the interplay between film formation dynamics and optoelectronic performance, particularly under fully ambient processing. While hot-air-assisted methods have shown great promise, challenges persist in achieving reproducible control over defect states, halide distribution, and long-term stability ¹¹⁰. Moreover, the influence of processing conditions on photoluminescence (PL) properties, important for quantifying non-radiative loss pathways, remains underexplored ¹⁰².

In this chapter, the role of slow cooling in controlling the structural and optoelectronic properties of $\text{CsPb}(\text{I},\text{Br})_3$ thin films fabricated under ambient conditions is systematically investigated. By analytically comparing solvent systems, cooling regimes, and subsequent device behaviour, the mechanisms by which thermal relaxation influences PL and charge recombination are elucidated. This work builds on the growing body of research into air-processed perovskites, providing new insight

into how slow cooling can be harnessed to achieve highly luminescent and stable all-inorganic perovskite films.

In this work, a warm-air-assisted, slow-cooling processing strategy is developed to fabricate $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin films entirely under ambient conditions. In contrast to the high-temperature hot-air processes commonly reported, this gentle approach produces films with intense and visibly intensified PL, together with greatly improved phase and emission stability. By systematically examining cooling dynamics, strain distribution, and oxygen incorporation, the factors that combine to suppress non-radiative recombination and influence interfacial energetics are identified. The insights gained establish slow-cooling not merely as a processing variable, but as a key lever to control both microstructure and optoelectronic behaviour in all-inorganic perovskites. This work therefore highlights a practical and scalable pathway towards photoluminescent, stable $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ devices whilst offering mechanistic guidance for future optimisation.

5.2 Fabrication Strategy

In this project, the precursor solution was prepared inside a nitrogen glovebox using a 2:1:1 molar ratio of $\text{CsI}:\text{PbI}_2:\text{PbBr}_2$ with a varying solvent mixture at a concentration of 0.5 M. The solution was heated and stirred at 60 °C for at least 2 hours to ensure complete dissolution. The resulting solution was then spin-coated in ambient air onto a glass substrate at 4000 rpm for 30 s while being continuously exposed to warm-air (50 °C, 5 m s⁻¹) using a heat gun to promote uniform film formation. The film was subsequently annealed on a hotplate in ambient air at 160 °C for 1 min and then cooled gradually to 40 °C at a rate of 5 °C min⁻¹. Finally, the sample was left on the switched-off hotplate until it reached room temperature.

5.3 Optimising Solvent Composition

In this study, solvent engineering was employed to investigate its impact on film formation and optical characterisation. *This was done* by systematically varying the ratio of dimethyl sulfoxide to dimethylformamide (DMSO:DMF) and N-methyl-2-pyrrolidone (DMSO:NMP) from pure DMSO to pure DMF or NMP, and examined the impact on the CsPbI_2Br film morphology, as shown in Figure 22a. The effect of the solvent on film coverage and continuity is evident in the SEM images. The *impact* of introducing NMP into pure DMSO was studied first. Although all warm-air-processed films show compact grains, the NMP-based films suffer from poor coverage. It is evident that coverage improves with increasing DMSO and reduced NMP content. The pure DMSO films exhibit improved coverage, but with extensive pinholes. Higher NMP content weakens Pb^{2+} coordination, resulting in fewer stable PbI_2 complexes and sparse nucleation. Although NMP's low viscosity promotes rapid spreading, its slow evaporation allows isolated grain growth, leaving gaps and pinholes.

In contrast, when partially substituting DMSO with DMF, the solution viscosity decreases, and although it remains slightly higher than in the DMSO:NMP system ^{143,144}, it is still low enough to enable uniform spreading. DMF's moderate coordination delays nucleation until after spreading is complete, and its faster evaporation accelerates supersaturation, leading to dense nucleation and the formation of a smooth, continuous film. This is reflected in the significantly reduced pinhole density, with the DMSO:DMF 1:3 (25 % DMSO and 75 % DMF) films exhibiting the most uniform and well-covered morphology. In contrast, the pure DMF film shows very poor film coverage, which, consistent with this explanation, is likely due to the extremely low viscosity and insufficient complexation, leading to premature nucleation.

The optical properties of the films change significantly as the processing solvent is varied, Figure 22b and c. Considering first the steady-state PL that shows several changes as the solvent composition is varied. Perhaps most notable are the changes in emission intensity and a broadening of the emission. Closer examination also reveals subtle shifts in the emission wavelength for the CsPbI₂Br composition driven by changes in the solvent composition, inset of Figure 22b. The highest emission intensities are observed for the DMSO:DMF compositions 1:1 and 1:3, with all other films having similar intensities, albeit with some non-systematic variance. Notably, the emission from the DMSO:NMP 3:1 film is extremely weak. Relative to the pure DMSO films, most samples exhibit a red-shifted emission, with the DMSO:NMP 1:3 film showing no shift. In addition, the sample prepared from pure DMF exhibited a blue-shift. Such red-shifts can be attributed to several factors, including local iodide enrichment arising from partial halide segregation or incomplete conversion, tensile strain within the lattice, higher absorption in thicker or more continuous films, or defect-induced bandgap renormalisation ^{108,145–147}. In contrast, the blue-shift observed may originate from Br-rich micro-regions, smaller grains exhibiting quantum confinement effects, compressive strain, or reduced dielectric screening because of improved defect passivation ^{148–150}. Considering the UV-Vis absorption data, a distinctly sharper absorption edge is seen in the DMSO:DMF 1:1 and 1:3 films. This can be partially explained by improved film coverage, which reduces substrate scattering and bleed-through. However, the parallel reduction in Urbach energy (UE) and the higher PL intensities suggest that the effect also reflects a genuine reduction in energetic disorder ¹⁵¹. Again, taking pure DMSO as the reference solvent, all films prepared, except that from pure DMF, show a blue-shift in the absorption onset (pure DMF shows a red-shift). Based on these results, a 3:7 DMSO:DMF ratio was selected, which is very close to the best-performing solvent composition of 1:3 DMSO:DMF. This choice was made to simplify the solution preparation process and to also comply with the literature, as the use of 30 % DMSO and 70 % DMF is more commonly reported than 25 % DMSO and 75 % DMF.

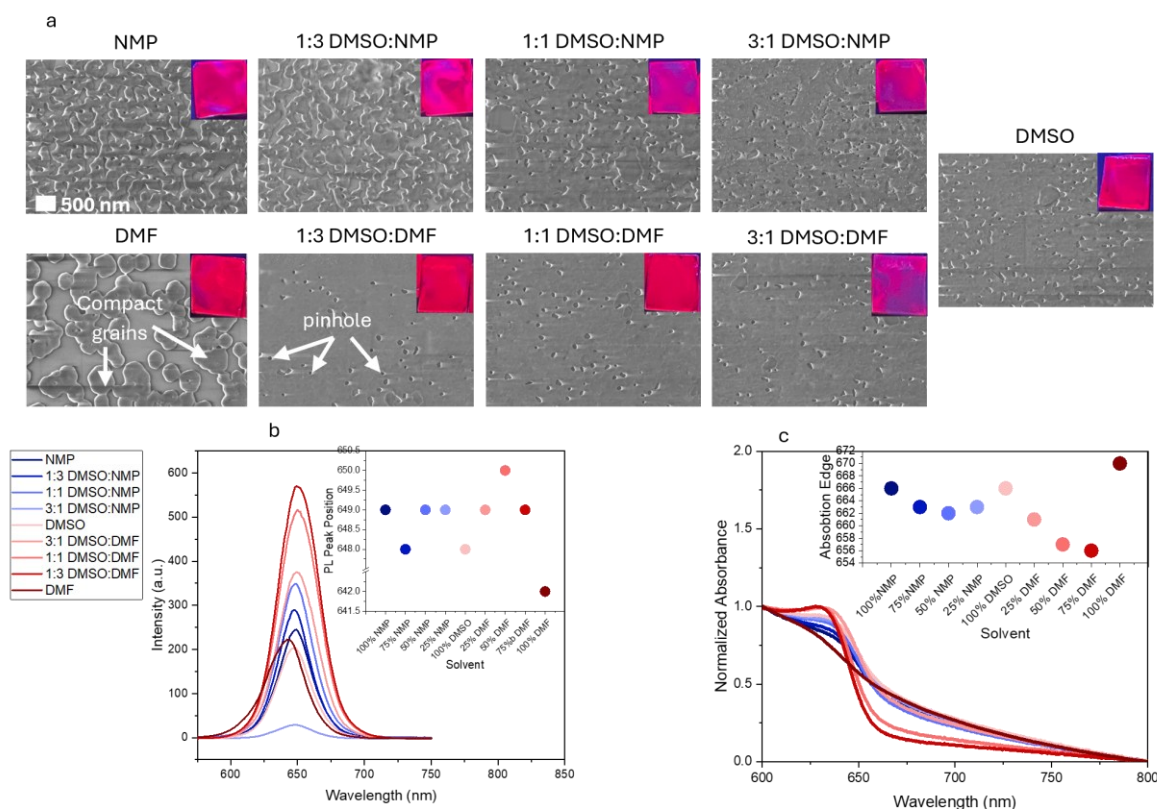


Figure 22 - Optical and morphological characterisation of CsPbI₂Br films fabricated using different DMSO–DMF–NMP solvent mixtures. (a) SEM images showing changes in film coverage, grain compactness, and pinhole formation with solvent composition; insets show the corresponding films under UV illumination. (b) Steady-state PL spectra with inset showing extracted peak positions, illustrating solvent-dependent changes in emission intensity and wavelength. (c) UV–Vis absorption spectra with inset showing calculated Urbach energies, indicating variations in absorption edge sharpness and energetic disorder with solvent composition.

5.4 Extending to Other CsPb(I,Br)₃ Compositions

To assess generality, the ability of the slow-cooling method to yield strongly photoluminescent films across other CsPb(I,Br)₃ compositions beyond CsPbI₂Br was investigated. The photographs under UV illumination (inset) show the expected colour progression from green (CsPbBr₃) → yellow (CsPbIBr₂) → orange (CsPbI_{1.5}Br_{1.5}) → red (CsPbI₂Br), matching the PL sequence (Figure 23a). CsPbI₃ was not investigated, as stabilisation of the photoactive α -phase remains unachievable under ambient conditions, in agreement with previous literature¹⁵². Some of the PL spectra exhibit broader emission peaks, often associated with partial halide segregation and structural defects; however, the peak positions and emission colours correspond well with the expected values for each composition^{153,154}. Approximate PL maxima are ~520 nm (CsPbBr₃), ~570–580 nm (CsPbIBr₂), ~600 nm (CsPbI_{1.5}Br_{1.5}), and ~650 nm (CsPbI₂Br), consistent with composition-dependent bandgap tuning. The

bandgap values obtained from Tauc plots, Figure 23b, of CsPbI₂Br (1.90 eV), CsPbI_{1.5}Br_{1.5} (2.00 eV), CsPbIBr₂ (2.14 eV), and CsPbBr₃ (2.35 eV) are consistent with the target compositions^{155–158}. The $(\alpha h\nu)^2$ onsets are linear over comparable ranges for all compositions, indicating direct-gap behaviour with similar sub-gap tailing, and the extracted E_g increases monotonically with Br content in agreement with the PL. The X-ray diffraction patterns reveal the presence of a preferred <101> orientation in all films with the anticipated 2 θ shift attributed to halide substitution observed in otherwise phase pure films, Figure 23c. Consistent with halide substitution, the diffraction peaks move to higher 2 θ with increasing Br content (lattice contraction), and no secondary phases are evident within the detection limit, the same trend is visible at the (100), (110), and (200) reflections. Slight peak broadening in the mixed-halide samples suggests comparable crystallite sizes with a small microstrain contribution. For the remainder of this study, the focus is on CsPbI₂Br.

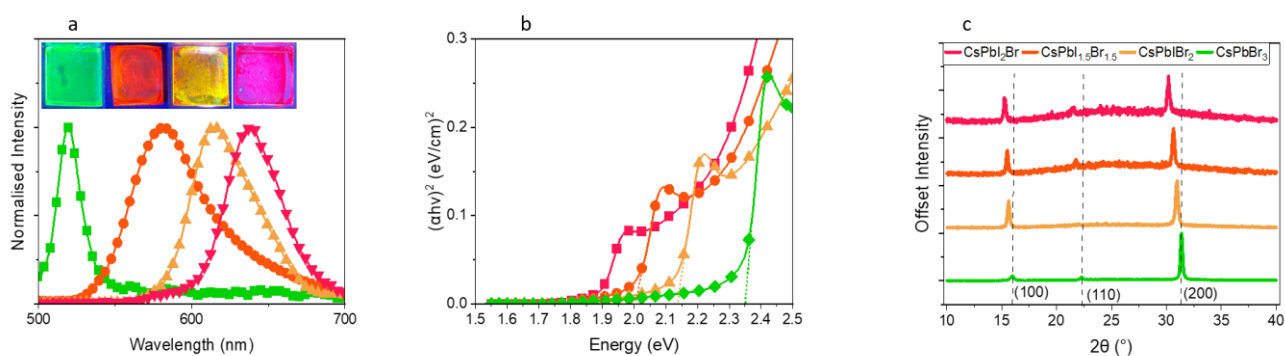


Figure 23 - Optical and structural characterisation of CsPb(I,Br)₃ compositions under the slow-cooling process: CsPbI₂Br (red), CsPbI_{1.5}Br_{1.5} (orange), CsPbIBr₂ (yellow), and CsPbBr₃ (green). (a) Steady-state photoluminescence spectra showing the systematic blue-shift in emission with increasing Br content; inset photographs show the corresponding films under UV illumination, confirming the colour progression from green to red. (b) Tauc plots derived from UV–Vis absorption data, showing direct bandgap behaviour and a monotonic increase in bandgap with Br incorporation, consistent with the PL trends. (c) XRD patterns of the films demonstrating phase purity, preferred <101> orientation, and systematic peak shifts to higher 2 θ with increasing Br content due to lattice contraction from halide substitution. No secondary phases are observed within the detection limit.

5.5 Warm-Air Processing Optimisation

Although the 1:3 DMSO:DMF films exhibit the best coverage among the solvent systems, the grain size remains limited. Because grain size is strongly governed by early-stage drying and solvent removal, we hypothesised that controlled warm-air exposure could promote film coalescence¹⁵⁹. To further improve the film coverage and increase grain size, the warm-air conditions were investigated.

Initially, films were exposed to warm-air during the total spin-coating duration (30 seconds). To probe how the onset of warm-air affects early-stage drying and coverage, we then varied the start time of

the treatment. Films were prepared with the warm-air treatment commencing after 0, 3, 7, and 10 seconds. All resulting films showed common grain features, namely a larger, continuous array of grains with smaller grains densely packed into the grain boundaries (Figure 24a). There was also a notable change in the dimensions of the larger grains, with the largest grains observed when warm-air treatment commenced 3 seconds into the spin-coating. It is known that initiating warm-air exposure before the optimum point leads to premature solvent removal and excessive nucleation, resulting in a less compact film composed of small crystallites at grain boundaries ¹⁶⁰. It is observed that longer delays (*i.e.* > 3 s) yield smaller grains, which could be because longer delays raise the density of nuclei formed before film drying. As these nuclei grow into grains, when the density is high, they will rapidly interact, hindering further growth and resulting in smaller grains separated by a higher density of boundaries ^{161 162}. In contrast, a delay of 3 seconds permits initial nuclei to stabilise so that the subsequent warm-air step favours growth over new nucleation, resulting in larger grains. Hence, a 3 s delay of warm-air exposure was chosen to process the results for the rest of the study. It is important to note that the SEM images in

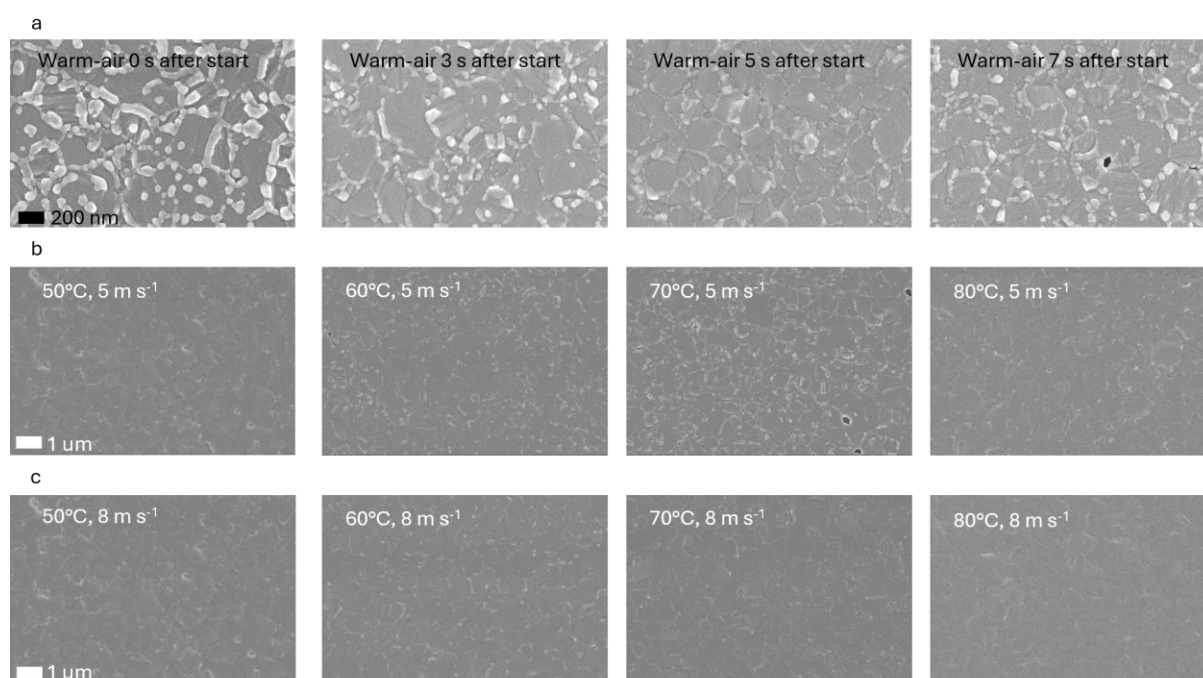


Figure 24a were obtained from films deposited on glass, which typically yields poorer film coverage. However, when deposited on [2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (a self-assembled monolayer, SAM, and common hole-transport material) on indium tin oxide (ITO/MeO-2PACz), the films display significantly improved coverage as illustrated in the following results, where all films were deposited atop ITO/MeO-2PACz substrate.

Subsequently, two additional variables were studied: the temperature and velocity of the warm-air treatment. Up until this point, samples have been processed using 50 °C warm-air with a speed of 5

m s^{-1} . In the first instance, temperature was varied from 50 - 80 °C in 10 °C increments, fixing velocity at 5 m s^{-1} . As shown in

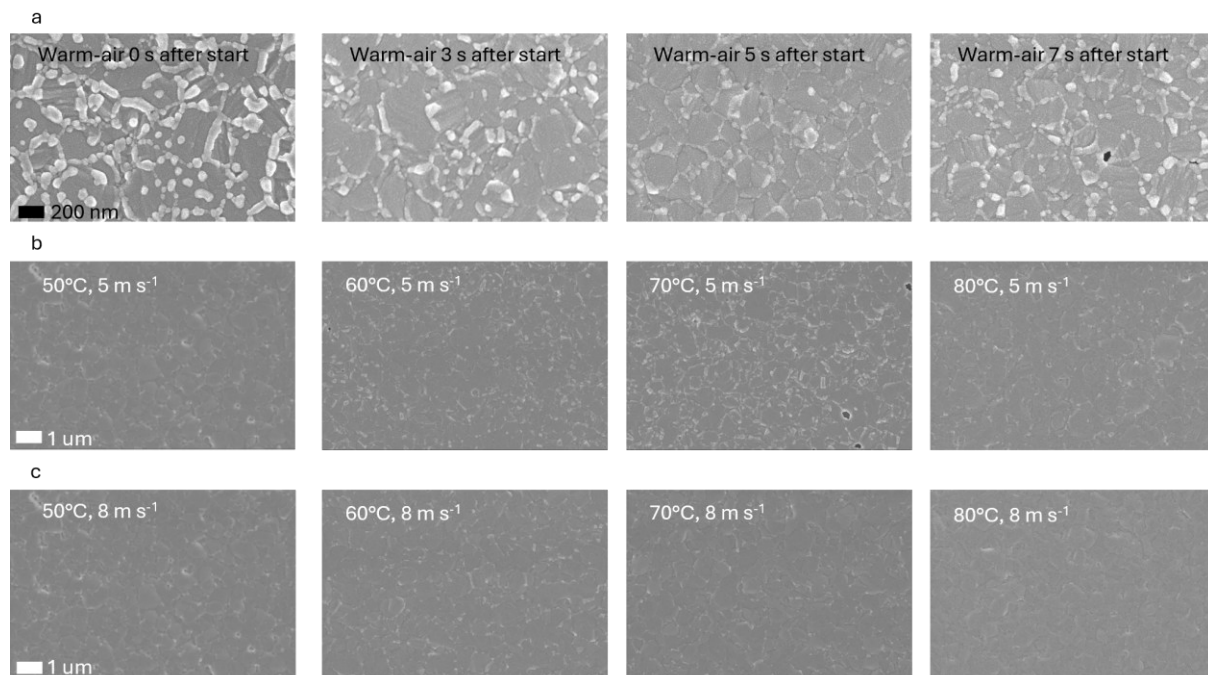


Figure 24b it was seen that lower temperatures produced more compact films, with fewer small crystallites seen at grain boundaries ¹⁶³. The same temperature range was again investigated; however, this time, the velocity was increased to 8 m s^{-1} (

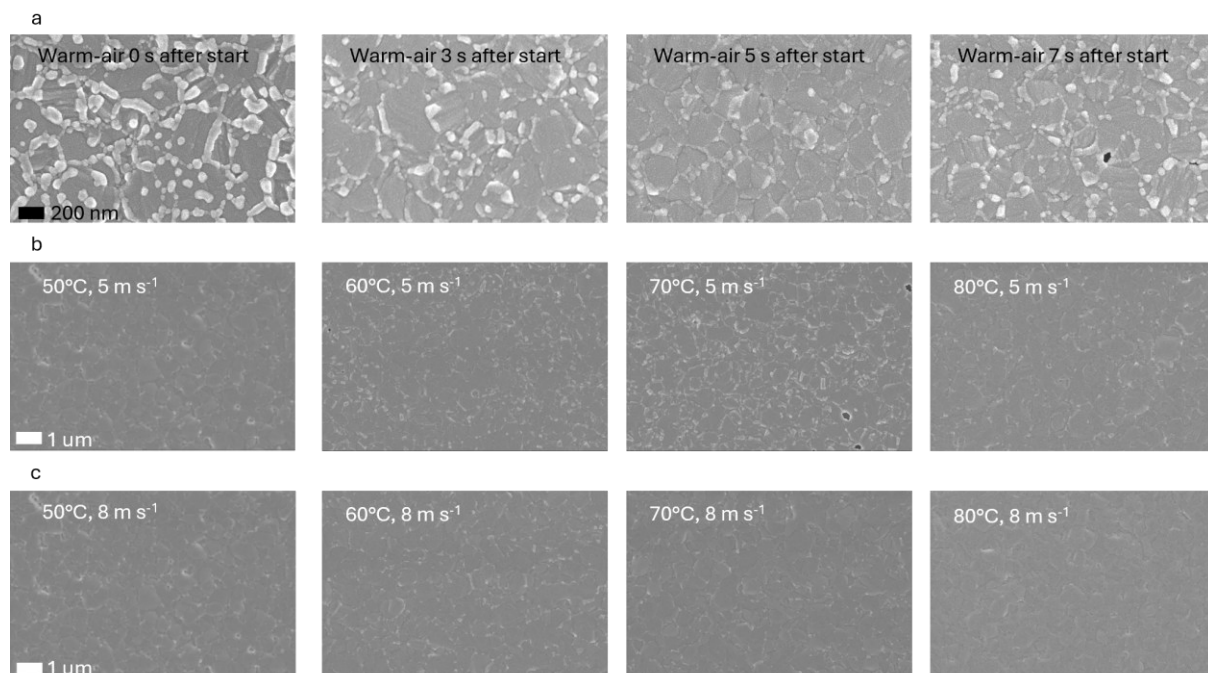


Figure 24c). In this case, compact, continuous films with large grains were formed with few small grains seen at the grain boundaries that are all independent of temperature ¹⁶⁴. This suggests that at low air speed, the process is heat-transfer-limited, meaning it is governed by how quickly heat from the warm-air can reach the wet film to supply the energy needed for solvent evaporation. Consequently, reducing the air temperature moderates solvent removal and suppresses secondary nucleation, yielding compact films with few boundary crystallites. In contrast, at the higher air velocity, the drying rate becomes dominated by airflow rather than temperature. Since the warm-air step favours grain growth over nucleation, the stronger airflow shortens the time window for additional nucleation, leading to compact films with similar morphologies across the tested temperature range ¹⁶⁵. Thus, in this system, the drying kinetics are primarily governed by air flow rather than by temperature. Therefore, the remainder of the work presented in this thesis relates to films that were processed with a warm-air temperature of 50 °C and a velocity of 8 m s⁻¹.

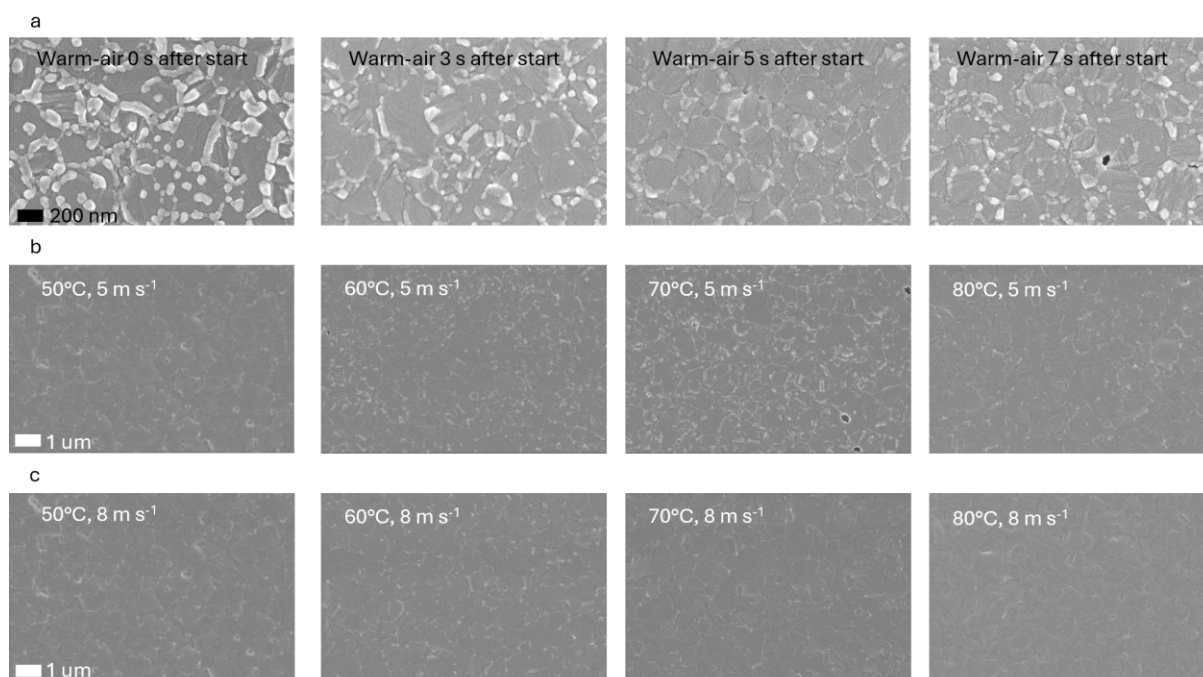


Figure 24 - SEM images illustrating the influence of warm-air processing parameters on CsPbI₂Br film morphology. (a) Effect of delaying the onset of warm-air exposure during spin-coating (0, 3, 5, and 7 s after the start), showing changes in grain size and boundary crystallites; these films were deposited on glass substrates. (b) Effect of warm-air temperature (50–80 °C) at a fixed air velocity of 5 m s⁻¹, demonstrating temperature-dependent changes in grain compactness for films deposited on ITO/MeO-2PACz. (c) Effect of warm-air temperature (50–80 °C) at a higher air velocity of 8 m s⁻¹, showing reduced temperature dependence and consistently compact films, also deposited on ITO/MeO-2PACz. Scale bars as indicated.

5.6 Solution Concentration and Deposition Sequence

Up to this point, all films were fabricated using a solution concentration of 0.5 M. In this section, the role of precursor concentration on film quality was also investigated, varying over the range of 1.0 to 0.25 M, as shown in Figure 4a. Films prepared from the highest two concentrations typically exhibited a significantly reduced number of pinholes. However, the visual appearance of films prepared using 1 M precursors was somewhat less reflective than those prepared at 0.75 M. Thus, the work was continued using 0.75 M solutions. A comparison was also made between one- and two-step deposition methods. In this case, the two-step involves the deposition of two successive layers of perovskite with a 60 s annealing (160 °C) between depositions. This results in the complete elimination of pinholes, as shown in Figure 4b. Notably, there is no appreciable increase in thickness when a two-step deposition is employed. This is explained by the solubility of layer one in the solvent used for layer 2, causing partial dissolution of layer 1. Additionally, the first layer serves as a seed layer, which also enhances the spread (wettability) of the substrate.

Combining the results obtained in the above sections, a set of processing conditions can now be defined that yields the best quality CsPbI₂Br films when processed fully under ambient conditions. Further results presented in this chapter rely on the use of a two-step deposition process, using a 50 °C warm-air treatment (8 m s⁻¹) during both deposition steps after 3 seconds into the spin coating process using 0.75 M precursor solutions (3:7 DMSO:DMF). These variables have been identified during this PhD project, rigorously investigated, and their impact on the optical, morphological and structural properties of perovskite thin films has been identified with a view to preparing high-quality films.

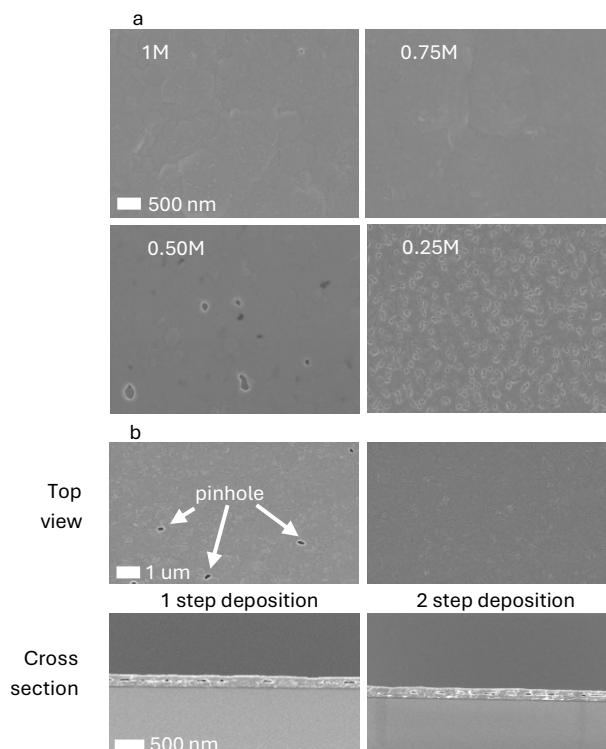


Figure 25 - Effect of precursor solution concentration and deposition sequence on CsPbI₂Br film morphology. (a) SEM images of films prepared using 1.0 M, 0.75 M, 0.50 M, and 0.25 M precursor solutions, showing an increase in pinhole density as concentration decreases, with 0.75 M providing the most uniform coverage. (b) Top-view and cross-sectional SEM images comparing one-step and two-step deposition (0.75 M), demonstrating elimination of pinholes without a significant increase in film thickness. Scale bars as indicated.

5.7 Controlled cooling of thermally annealed perovskite films

The results presented thus far have been obtained from films thermally annealed to 160 °C during processing, then slowly cooled by ramping down the temperature of the hotplate to 40 °C. Early in the PhD this was identified as a critical step because without controlled cooling, the cooling rate depends on the room temperature, which changes with the weather and leads to varying results. Here, more precise control of cooling is obtained using an *in-situ* heating controller inside an X-ray diffractometer, whereby XRD data were obtained during a slow (5 °C min⁻¹) cooling from 160 to 40 °C.

The resulting XRD data, Figure 26a, show the (100), (110), and (200) peaks corresponding to the photoactive α -phase of CsPbI₂Br, with no additional phases detected. As observed previously, the films exhibit a preferred <100> orientation, and all peaks show a systematic shift to higher 2 θ position when cooled, as shown in Figure 26b as well. This shift is almost linear and can indicate a consistent lattice contraction rate ^{103,149}. It is important to note that potential artefacts arising from thermal

expansion or contraction of the sample stage were carefully considered. The sample alignment was performed at 160 °C prior to initiating the cooling scan, and the alignment was rechecked after the film returned to room temperature. No measurable change in alignment was observed between these two conditions, indicating that the sample position relative to the X-ray beam remained constant throughout the experiment. This confirms that the observed peak shifts originate from intrinsic lattice changes within the film rather than mechanical movement or thermal expansion of the stage. In principle, any stage-induced shift could be quantified by repeating the measurement on a strain-free reference material (e.g., Si) under identical thermal conditions; however, the absence of alignment change in this experiment indicates that such contributions are negligible here. The shift in peak position indicates that the tensile strain becomes more negative as the temperature decreases, suggesting the development of compressive strain in the films. This is almost linear for all three diffraction peaks across the temperature range Figure 26c¹⁰³. Analysis of the effective full width at half-maximum (effective FWHM) of all three diffraction peaks shows similar behaviour, Figure 26d. A subtle reduction in effective FWHM when cooled from 160 to 140 °C followed by a steady increase. In all cases, the effective FWHM at 40 °C is greater than at 160°C. Hence, the corresponding microstrain follows a similar trend and transitioning point at 140°C, Figure 26e. The overall dropping (Figure 26f) intensity trend can be attributed to a reduction in crystallinity caused by the build-up of compressive strain and the accompanying rise in microstrain and effective FWHM (peak broadening), which reduces coherent scattering rather than indicating secondary phases.

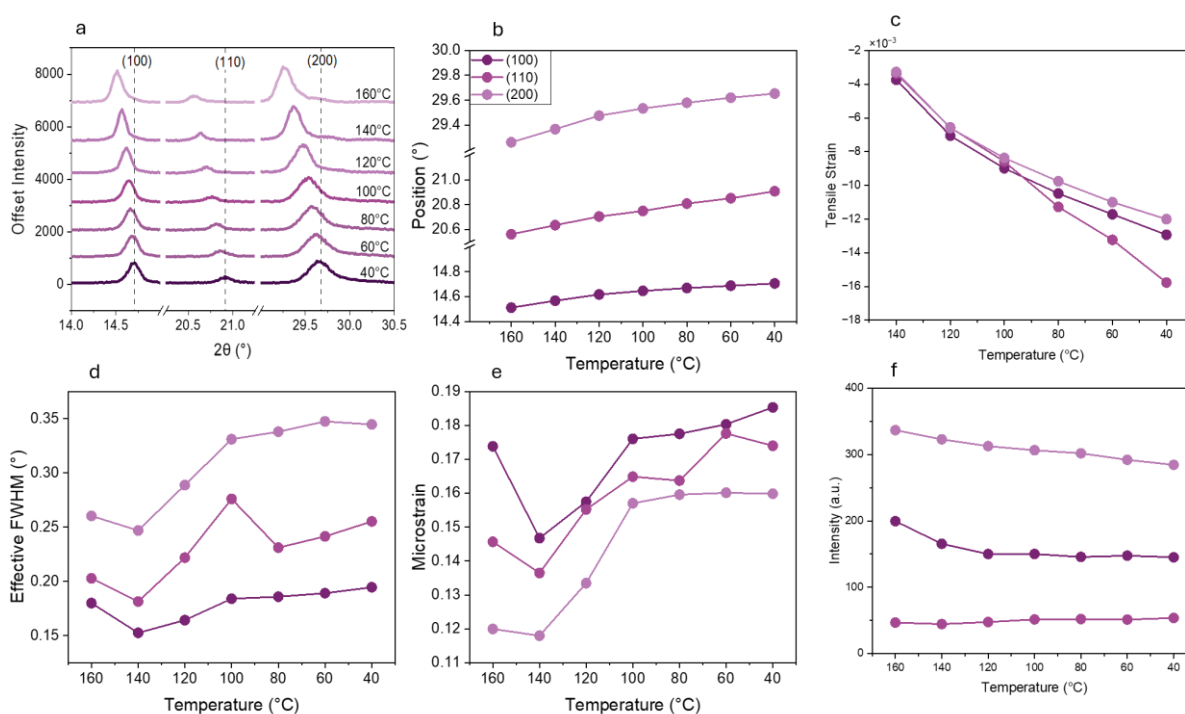


Figure 26 - In situ XRD analysis of CsPbI₂Br films during controlled cooling at 5 °C min⁻¹ from 160 °C to 40 °C. (a) Stacked diffraction patterns showing the (100), (110), and (200) reflections of the α -

phase and their systematic shift with decreasing temperature. (b) Peak position as a function of temperature, showing an approximately linear shift to higher 2θ . (c) Corresponding tensile strain evolution derived from peak positions. (d) Effective FWHM (integral breadth) of the three peaks, indicating peak broadening during cooling. (e) Microstrain calculated from the effective FWHM, showing a transition around 140 °C. (f) Peak intensity variation with temperature, reflecting changes in coherent scattering during cooling.

An additional comparison was made between two films that were treated differently following thermal annealing at 160 °C. A slowly cooled film was controllably cooled on the hotplate from 160 to 40 °C over a period of ~25 mins, and a rapidly cooled sample was directly removed from the hotplate after 10 mins and left to cool. The XRD patterns of both films are shown in Figure 27a, with the slowly cooled sample showing a slight increase in the intensity of the diffraction peaks and a subtle reduction in FWHM, indicating improved crystallographic order. Notably, the slowly cooled film also exhibits a shift in peaks positions to higher 2θ than the rapidly cooled film, indicating a smaller out-of-plane d-spacing at room temperature. Consistent with the *in-situ* cooling data, this corresponds to a more negative (compressive) residual lattice strain in the slowly cooled film. In contrast, the rapidly cooled film retains a slightly expanded lattice and therefore a less compressive residual strain.

As illustrated in Figure 27b-c, we performed the grazing incidence X-ray diffraction (GIXRD) on these two samples. The position, tensile strain, Intensity, effective FWHM, and microstrain were accordingly traced as a function of depth, Figure 27d-h. The position of the (110) peak remains fixed as the grazing angle is varied, however, the (100) and (200) peaks generally shift to lower (2θ) positions as the incident angle (ω) is increased, Figure 27d. Arguably the slowly cooled films show a lesser shift in position in comparison to rapidly cooled (100) and (200) peaks. This is attributed to tensile strain trapped near the surface of rapidly cooled films that gradually relaxes with increased depth, while the slowly cooled film remains uniform and strain-relieved¹⁰³. It is noted, as shown in Figure 27e, that there are transitioning ω values for both samples where the trends of both the peaks positions and their tensile strain changes. These transitioning points are 2.5° for slowly cooled sample and 5° for rapidly cooled samples. At ω values below these transitioning points, the tensile strain is maximum and begins to reduce as ω increases. The reduction in tensile strain beyond these ω values is more pronounced in the slowly cooled sample and less significant in the rapidly cooled sample. This behaviour indicates that, in the rapidly cooled films, strain is strongly localised near the surface and relaxes gradually with depth, whereas the slowly cooled films exhibit a more uniform strain distribution through the thickness. In Figure 27f, the intensity is also tracked. It is important to note that, in GIXRD rocking-curve geometry, the diffracted intensity is constrained by the θ – 2θ condition, where diffraction from a given set of planes is only geometrically favoured while the incidence angle ω remains comparable to or smaller than the Bragg angle θ of that reflection. As ω approaches or exceeds θ , the effective diffracting volume for that reflection decreases, leading to a reduction in measured

intensity irrespective of microstructural changes. Therefore, variations in peak intensity with ω cannot be interpreted solely as changes in crystallinity, texture, or phase fraction, but must be considered alongside this geometric limitation. Hence, the variation in relative intensities of the (100) and (200) peaks with ω should be interpreted as a combination of depth-dependent strain relaxation and the changing geometric accessibility of these reflections. At low ω , reflections with smaller θ (such as (100)) are favoured due to a larger effective diffracting volume, whereas at higher ω , reflections with larger θ (such as (200)) become more geometrically favoured, giving the appearance of an intensity crossover.^{149,103} As expected, for the effective FWHM and microstrain (Figure 27g-h), similar trends are observed. Both show a reduction with increasing ω , indicating larger crystallites and reduced strain at deeper layers¹⁰³, while also reflecting the improved geometric fulfilment of the Bragg condition as ω approaches the Bragg angle θ for these reflections.

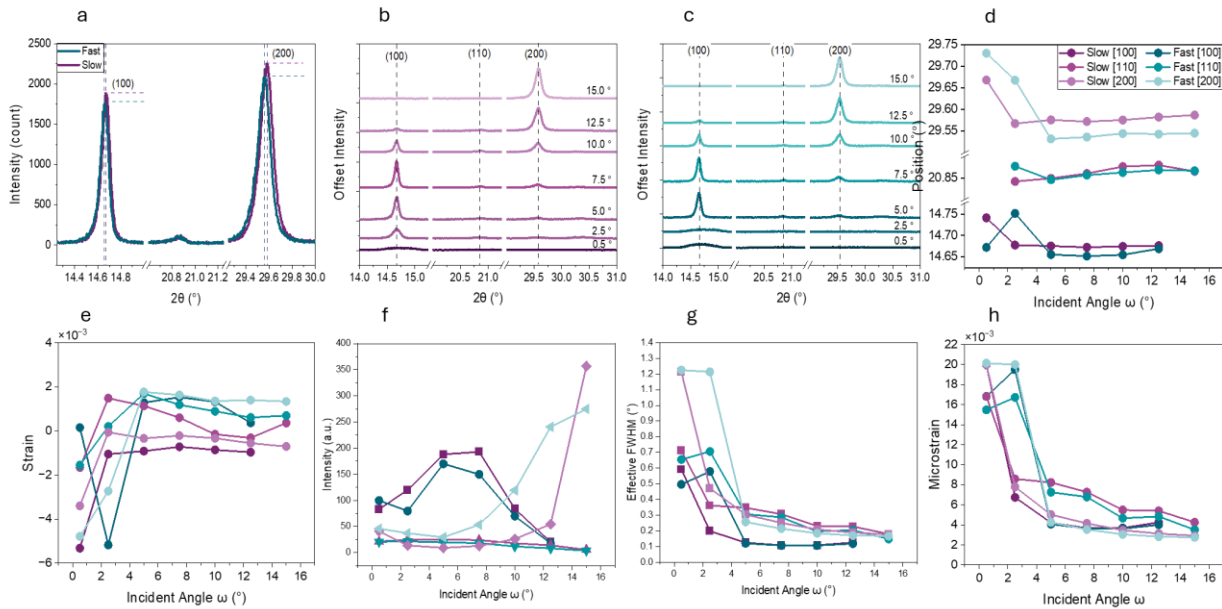


Figure 27 - Comparison of crystallographic behaviour in rapidly and slowly cooled CsPbI₂Br films. (a) Conventional XRD patterns showing slightly sharper peaks and a shift to higher 2θ for the slowly cooled film. (b–c) Stacked GIXRD scans for the slowly cooled and rapidly cooled films, respectively, showing the (100), (110), and (200) reflections as ω is varied. (d–h) Parameters extracted from the GIXRD data as a function of grazing incidence angle ω : (d) peak position, (e) calculated tensile strain, (f) peak intensity, (g) effective FWHM (integral breadth), and (h) microstrain, illustrating depth-dependent strain relaxation and geometric effects inherent to the GIXRD configuration.

5.8 Surface Chemistry and Electronic Properties

Using ambient photoelectron spectroscopy (APS) and Kelvin probe (KP) the valence band energy and Fermi level of the rapidly- and slowly-cooled samples were measured. Both have the same E_g energy, around 1.9 eV, which is comparable to CsPbI₂Br prepared under inert conditions¹⁵⁷. The ambient-air-processed samples have lower ionisation potentials and electron affinities *i.e.* Conduction band minimum (CBM) and valence band maximum (VBM) are shifted upwards towards the vacuum level (Figure 28a)^{166–168}. The rapidly cooled sample shows a shallower E_{VBM} , -5.12 eV, while the slowly cooled sample has a deeper E_{VBM} , -5.35 eV. Correspondingly, the E_{CBM} lie at -3.22 eV and -3.45 eV for the rapidly and slowly cooled samples, respectively. The Fermi level of the ambient-air-processed samples is shifted much closer to the VBM as a result of doping, possibly due to oxygen incorporation into the crystal structure^{169–172}. The energy difference $E_F - E_{VBM}$ is 0.39 eV for the rapidly cooled film and 0.28 eV for the slowly cooled film. This suggests greater doping in the slowly cooled sample, that can be attributed to greater oxygen incorporation enabled by the elevated high temperature exposure.

X-ray photoelectron spectroscopy (XPS) was used to analyse the near-surface composition of the slow- and rapidly cooled samples, Figure 28b-e. The signals for Pb 4f, Cs 4d, I 3d and Br 3d are very similar across both sample types indicating similar overall surface chemistry and composition. The Pb 4f spectra for both samples show two distinct Pb environments, a dominant Pb-lattice signal and a lower intensity Pb-O signal. Whilst the Pb-lattice doublets are seen at 143 and 138 eV for both, there is a notable shift in the binding energy (BE) of the Pb-O signals. The slowly cooled sample shows a slightly lower oxide-related Pb 4f binding energy than the rapidly cooled sample (by ~0.3-0.5 eV), which we attribute to a relatively lower effective oxidation state (more PbO-like). In the O 1s spectra, Pb-O, O-H, and H₂O are seen in both samples, Figure 28f. The absolute O 1s intensity is higher for the slowly cooled film, but the fractional H₂O/O-H is higher in the rapidly cooled film. In the slowly cooled film, the O 1s envelope is centred near ~531.2 eV, which corresponds to surface OH/H₂O; lattice Pb-O would be expected at lower binding energy (~529-530 eV), and Pb 4f lies in the 138-143 eV range. Overall, the higher fractional H₂O/O-H in the rapidly cooled film and the slightly lower oxide-related Pb 4f BE in the slowly cooled film are consistent with a relatively less hydroxylated, more lattice-oxide-like surface after slow cooling¹⁷³.

Angle-resolved XRS (ARXPS) has been also performed over the angles 10, 15, 30, 45, 60, 75, and 90 degrees where the emission angle is measured from the surface normal so 10° corresponds to the most depth-weighted scan and 90° to the most surface-weighted scan. Figure 28 g-i together indicate a clear vertical chemical gradient in both films, with the cooling protocol strongly affecting its magnitude. In the slow-cooled film (Figure 28g), the O 1s signal is highest at the most surface-weighted angles and decreases toward the depth-weighted conditions, consistent with a surface-localised oxygen contribution (e.g., adsorbed oxygenated species and/or superficial Pb–O formation

during air exposure). In contrast, Pb 4f and Br 3d signals generally become stronger as the scan becomes more depth-weighted, while Cs 3d shows the opposite trend, indicating that the near-surface region is relatively Cs-enriched and Pb/Br-depleted, with a more Pb/Br-rich composition toward the bulk. The fast-cooled film (Figure 28h) shows the same directional behaviour but with a stronger gradient, suggesting that rapid cooling kinetically “freezes in” a sharper vertical segregation profile.

Figure 28i links these compositional trends to Pb chemical evolution using the corrected Pb oxidation fraction: the slow- and fast-cooled films exhibit different oxidation levels and/or angle dependences, indicating that Pb oxidation is coupled to the near-surface oxygen signal rather than the bulk composition. Mechanistically, these trends are consistent with oxygen uptake being predominantly a surface process during cooling in air, while the Br/Pb vs Cs redistribution reflects depth-dependent crystallisation/relaxation and ion mobility during the cooling step. Overall, slow cooling provides more time for chemical relaxation that can reduce extreme compositional gradients, whereas fast cooling limits redistribution and retains a more abrupt depth profile; any Pb–O formation remains primarily confined to the surface-weighted region sampled at high emission angles.

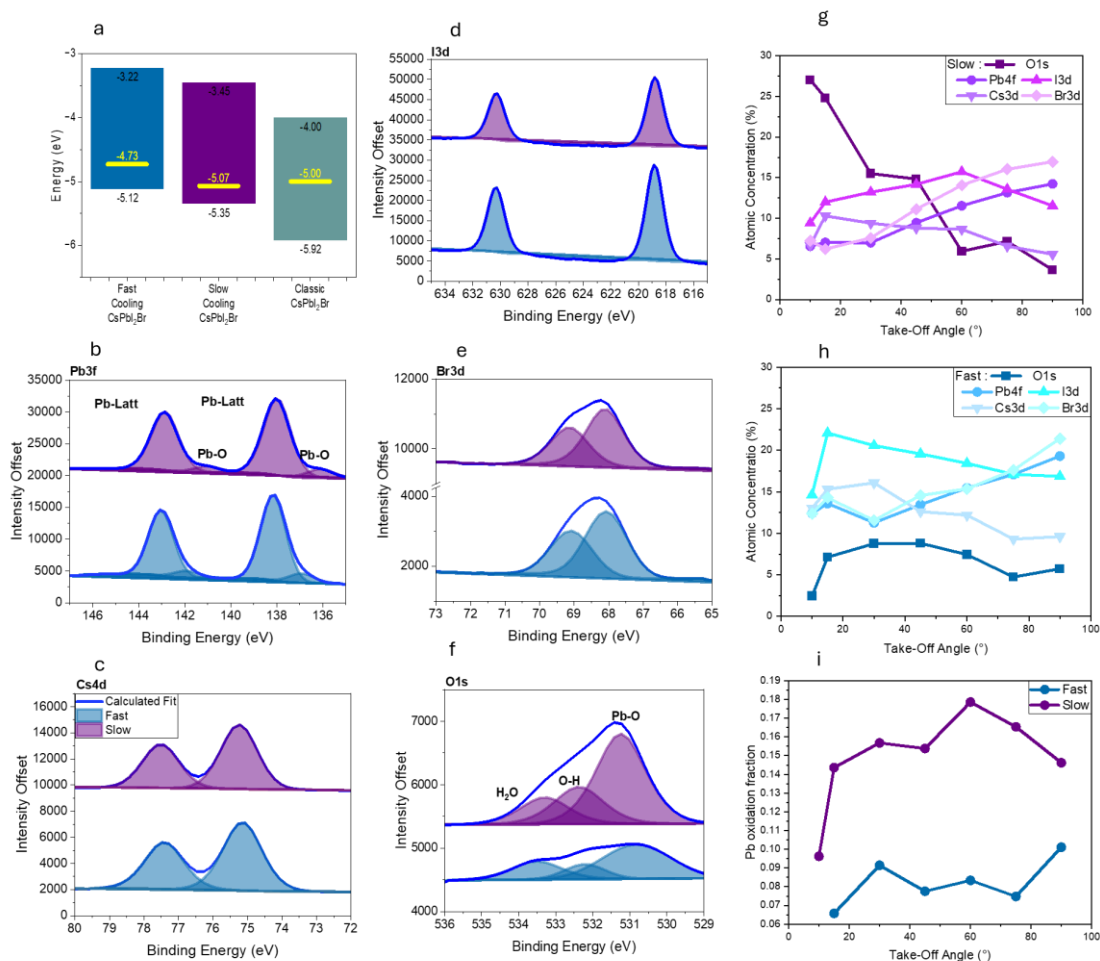


Figure 28 - Band alignment and surface chemistry of rapidly and slowly cooled CsPbI₂Br films. (a) Band alignment derived from APS and Kelvin probe measurements, with literature values for N₂-processed CsPbI₂Br shown for comparison. High-resolution XPS spectra showing (b) Pb 4f deconvolution into Pb-lattice and Pb–O components, (c) Cs 4d, (d) I 3d, (e) Br 3d, and (f) O 1s deconvolution into Pb–O, O–H, and H₂O contributions. Angle-resolved XPS (ARXPS) showing atomic concentration as a function of emission angle for the (g) slowly cooled and (h) rapidly cooled films. (i) Fraction of oxidised Pb as a function of emission angle, linking Pb chemical state to the near-surface oxygen distribution.^{166,167,174}

5.9 Role of Oxygen Incorporation and Cooling Rate

The previous results suggest very distinct O-incorporation, which may be the result of the different samples being exposed to air under 160°C annealing temperature for different times. To fully understand the O-incorporation into the surface of the film as a function of time, the annealing time under the rapid-cooling condition was varied to 10, 20, and 30 min and compared to the classically slowly cooled sample optimised in this study, while keeping all other parameters constant. Following

the establishment of the fabrication conditions, the effect of oxygen incorporation differences on the films' photoluminescence behaviour was investigated.

To understand the influence of oxygen doping and cooling rate on PL, different fabrication conditions were tested: films annealed at 160 °C for 10, 20, and 30 min and then rapidly cooled by removing them directly from the hotplate, as well as films slowly cooled from 160 °C to 40 °C at a rate of 5 °C min⁻¹. The fastly cooled samples are referred to by their annealing times (10-, 20-, and 30-min samples). To further investigate the interaction of these films with transport layers in p-i- devices, perovskite films fabricated under the stated conditions were deposited on three substrates: bare glass, MeO-2PACz-modified ITO-coated glass, and glass where the perovskite layer was subsequently coated with a thin layer of C₆₀. The excitation wavelength was 404 nm, and data were collected for both front- and back-side excitation. In all cases, the PL signal from the slowly cooled film was approximately an order of magnitude greater than that of any comparable rapidly cooled sample, and the PL intensity for all samples excited from the back side (*i.e.*, PL originating from the buried interface of the perovskite) was higher than when excited from the front side (Figure 29a-d). As expected, both C₆₀ and ITO/MeO-2PACz act as strong PL quenchers, with the latter being a very efficient quenching layer. The fullerene layer also exhibits strong quenching under front-side illumination. However, it is important to note that C₆₀ absorbs a portion of the excitation light, making this geometry less ideal for assessing intrinsic quenching (Figure 29a). In C₆₀-capped samples excited from the back side, a feature near 670 nm was observed, particularly in the 10-, 20-, and 30-min samples. This coincides with the C₆₀ absorption edge (Figure A 3 in Appendix II), indicating that PL from the perovskite is partially reabsorbed by C₆₀ at wavelengths below 670 nm, and the observed emission corresponds to the tail of the spectrum at energies below the bandgap of C₆₀. It should also be noted that in the slowly cooled samples, there were very subtle shifts in the PL peak position between front- and back-side excitation. These shifts may be attributed to the changes in surface electronic properties and composition identified in earlier analysis. However, the magnitude of these changes and their implications are considered beyond the scope of this work.

In an attempt to compensate for the parasitic absorption losses in the PL scans of samples capped with C₆₀, PL measurements were paired with UV-Vis spectroscopy to calculate the Urbach energy (UE). Five positions were measured per sample, and the absorption spectra were averaged to obtain a representative mean UE value. The UE values for the four films prepared under the specified fabrication conditions are shown in Figure 29e-h, again using films prepared on glass, ITO/MeO-2PACz, and capped with C₆₀. For most samples, the calculated UE is highest for the bare-glass substrate, indicating more tail states and greater energetic disorder. The inclusion of ITO/MeO-2PACz and C₆₀ lowers UE in the rapidly cooled samples, as reflected by the sharper absorption onset compared to films deposited on bare glass. However, no consistent trend is observed across all samples. Whilst it is likely that the SAM is impacting the microstructure and homogeneity of the buried

interface, resulting in a “cleaner” interface with fewer electronic defects, this explanation is less likely for the C₆₀ interface since the fullerene is deposited after perovskite formation.

Excitation-intensity-dependent time-correlated single-photon counting (TCSPC) provides deeper insight than measurements at a fixed excitation intensity, as it reveals how different recombination pathways compete and evolve with excitation density. By varying excitation intensity, intrinsic effects such as trap filling can be distinguished from extrinsic influences, and nonlinear processes such as trap saturation and Auger recombination can be uncovered, which remain hidden under constant excitation. Therefore, excitation-intensity-dependent TCSPC was performed on the same sample set, tracking the average lifetimes (τ_1 , τ_2 , τ_3) and the tri-exponential weights (A_1 , A_2 , A_3): A_1 (τ_1 , fast) corresponds to non-radiative capture, A_2 (τ_2 , intermediate) to shallow-trap-mediated transfer, and A_3 (τ_3 , slow) to bulk radiative recombination. All samples show an increase in average lifetime with excitation intensity (Figure 29**Figure 29i**). This behaviour is consistent with trap filling at higher carrier densities, which suppresses non-radiative pathways and prolongs the effective lifetime. The increase is noticeably smaller for the rapidly cooled films compared with the slowly cooled film, which also shows more pronounced front/back differences, with the front-illuminated sample exhibiting a shorter lifetime. Overall, A_1 decreases with increasing excitation intensity, suggesting reduced non-radiative recombination via trap filling or defect passivation at higher carrier densities, Figure 29j. For the rapidly cooled samples, front excitation consistently yields a higher non-radiative weight (A_1) compared with back excitation. The weight of A_1 is significantly lower in the slowly cooled sample than in any of the rapidly cooled samples, indicating improved bulk defect passivation. For A_2 , Figure 29k, distinct behaviours are observed: A_2 increases with excitation intensity for the 30 mins sample, decreases gradually for the 20 mins and slowly cooled samples, and drops sharply for the 10 mins sample. The difference in A_2 between front- and back-side excitation widens with intensity for the 30 mins sample but narrows for the 10 mins sample, suggesting a non-uniform shallow-trap distribution that depends on carrier density, with the surface likely having fewer shallow traps, possibly due to oxygen passivation. The 20 mins sample shows a more uniform shallow-trap-assisted recombination profile. In the slowly cooled sample, the front/back difference in A_2 remains nearly constant across excitation intensities, indicating a stable shallow-trap distribution, with A_2 consistently higher at the front. Consistent with suppressed non-radiative loss, A_3 (the slow, radiative channel) increases with excitation intensity and is systematically higher for the slowly cooled film than for the rapidly cooled films (Figure 29l), indicating a larger fraction of carriers recombine radiatively.

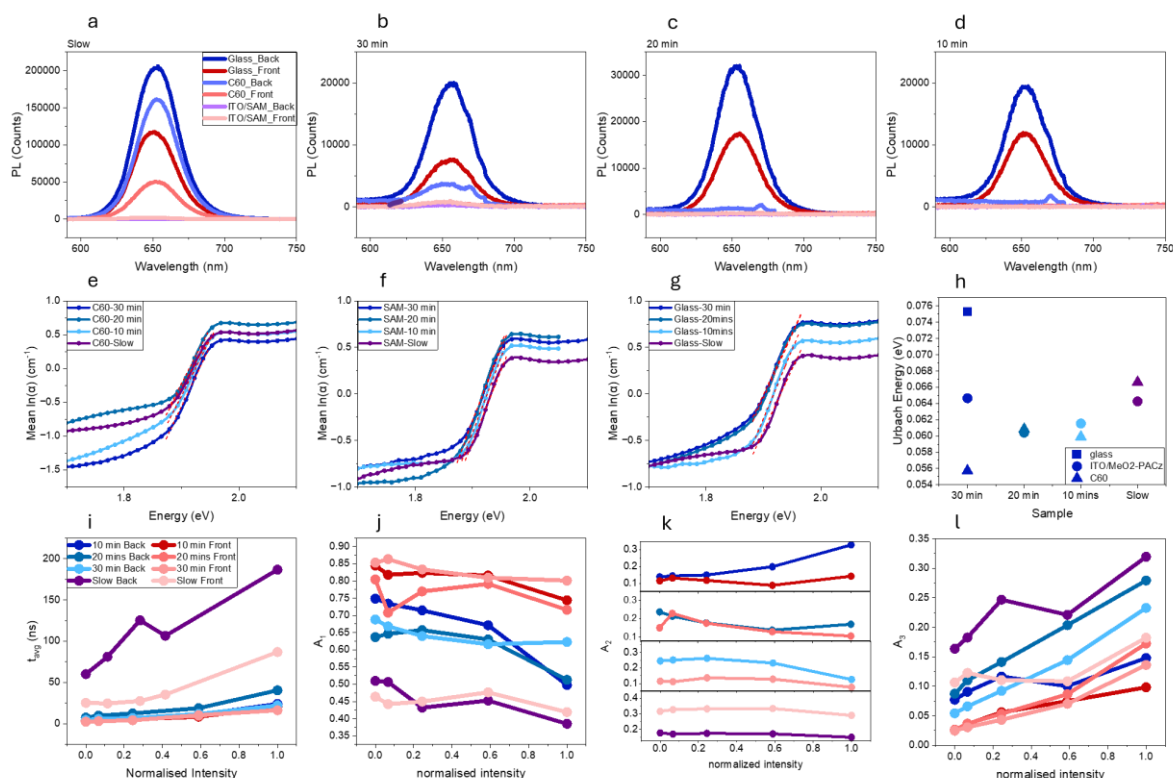


Figure 29 - PL of CsPbI₂Br under 404 nm excitation vs cooling/stack: (a) slowly cooled, (b) fast-30 min, (c) fast-20 min, (d) fast-10 min spectra for front and back excitation. The slowly cooled film shows significantly higher PL intensity, while ITO/MeO-2PACz and C₆₀ act as strong quenchers; a feature near ~670 nm in C₆₀-capped samples arises from partial reabsorption of perovskite emission by C₆₀. Urbach-tail analysis: mean ln(α) vs energy for films on (e) C₆₀, (f) ITO/MeO-2PACz, and (g) glass. (h) Mean Urbach energy, showing generally lower energetic disorder when transport layers are present, particularly for rapidly cooled samples. Excitation-intensity-dependent TCSPC of CsPbI₂Br films (front vs back): (i) average lifetime (τ_{av}), (j) A₁ fraction (τ₁, non-radiative), (k) A₂ fraction (τ₂, shallow-trap), and (l) A₃ fraction (τ₃, radiative) for 30 min, 10 min, 20 min, and slowly cooled films as functions of excitation intensity. The slowly cooled film consistently shows longer lifetimes, reduced non-radiative contribution, and enhanced radiative recombination compared with rapidly cooled films, indicating improved defect passivation and more uniform recombination behaviour.

5.10 Stability Under Ambient Conditions

To assess the stability of the films prepared, *in-situ* UV-Vis and PL measurements were carried out at 25 °C and 50 % relative humidity (RH). The evolution of absorption and emission peaks as a function of time is shown in Figure 30. From the absorption data (Figure 30a-d), it is inferred that most changes occur within the first few minutes. The film annealed for 10 min shows the lowest stability, with a phase change observed after only ~2 min. This phase change is indicated by a shift in absorption from around 650 nm to around 500 nm. The other samples exhibit longer phase stability

but show a drop in absorption intensity, which could be indicative of a partial phase change. Specifically, after 2 min, the absorption intensity of the 20 min and 30 min samples is reduced by ~55 % and ~74 %, respectively. In contrast, the slowly cooled film shows no change even after 300 min of testing, demonstrating considerably improved stability.

This behaviour is mirrored in the PL data (Figure 30e-h): in the 10 min sample, emission is observed only for a few minutes, consistent with a rapid transition from the α - to δ -phase. The emission behaviour in the 20 min and 30 min films is unusual: both show intense PL for the first 5-10 min, which then drops in intensity before recovering. For both samples, the initial drop occurs by around 50 min into the measurement, followed by recovery. The 20 min sample reaches maximum emission lasting for 10-15 min at around 200 min, whereas the 30 min film reaches maximum intensity around 100 min and maintains it for nearly 100 min. In both cases, the emission intensity then decays at a rate similar to the preceding rise. It is speculated that this rise-fall behaviour reflects a competition between defect passivation and the onset of phase change observed in the absorption spectra. This behaviour is not observed in the slowly cooled sample (Figure 30h). During the first 175 min, this sample exhibits a gradual increase in PL intensity accompanied by spectral broadening. The broadening then stabilises while the intensity continues to increase steadily throughout the 300 min measurement.

Consequently, it is likely that the 10 min annealing step does little to passivate electronic defects and traps; hence emission quenching is rapid. Annealing for 20-30 min results in partial recovery of emission, attributed to the interplay between defect passivation and phase change. Slow cooling results in excellent phase stability, as evidenced by the steady absorption and strong, sustained PL emission.

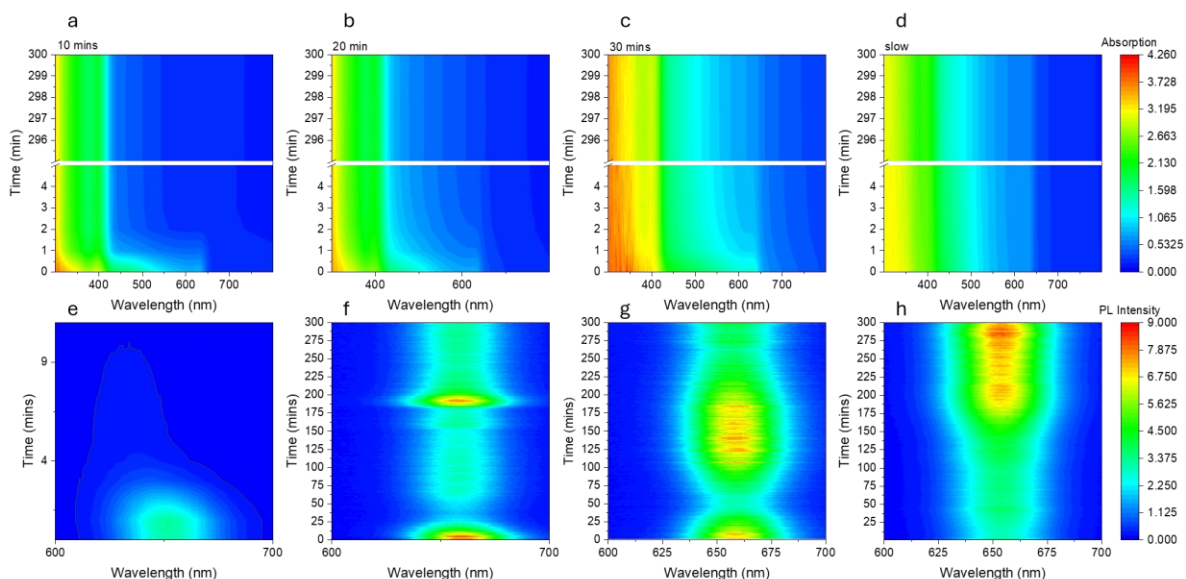


Figure 30- *In-situ stability of CsPbI₂Br films in ambient air (25 °C, ~50 % RH). (a–d) Time–wavelength absorption maps and (e–h) corresponding PL maps for films annealed for 10 min, 20 min, 30 min, and slowly cooled, respectively. Rapid spectral shift from ~650 nm to ~500 nm in the 10 min film indicates fast $\alpha \rightarrow \delta$ phase transition. The 20 and 30 min films show initial intensity loss followed by partial recovery before gradual degradation, whereas the slowly cooled film maintains stable absorption and steadily increasing PL over 300 min, demonstrating superior phase and electronic stability.*

5.11 Photovoltaic Device Performance

Following the previous results, we fabricated devices for all four conditions. The device of the structure ITO/MeO-2PACz/CsPbI₂Br/C₆₀/BCP/Ag was fabricated as described in the experimental method chapter. Current density-voltage (JV) analysis, external quantum efficiency (EQE), and electrochemical impedance spectroscopy (EIS) were conducted and analysed.

Statistical data for device power conversion efficiency (PCE), open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) are shown in the box plots in Figure 31a-d. From these data, the optimum condition appears to be the 20 min anneal, as it gives rise to the highest PCE, V_{oc} , and J_{sc} values, and shows the least statistical variation across all performance metrics. The external quantum efficiency (EQE) of the 20 min sample is also shown in Figure 31e, with the integrated current density being slightly lower than the statistical average J_{sc} . Surprisingly, the slowly cooled sample showed less reproducibility and lower performance overall, despite its superior film quality and stability.

Next, to understand the origins of this unexpected result, transient photovoltage (TPV) and transient photocurrent (TPC) were carried out. TPV should provide insight into charge-carrier recombination, whilst TPC should highlight differences in the rate and completeness of photocarrier extraction. However, the data obtained for both measurements showed no significant differences between any of the samples (Figure A 4 in Appendix II). The low PCE of the slowly cooled devices can be correlated with the very poor J_{sc} values obtained, indicating that charge extraction is limited in these devices (Figure 31c). This could be correlated with the depth-dependent O-doping of the sample, which alters the energetic alignment at the perovskite:C₆₀ interface as reported by APS/KP measurements. This may also be explained by the subtle compositional changes indicated by ARPES and GIXRD (*e.g.*, microstrain or preferred orientation changes), or indeed a combination of these factors.

Interesting changes in device hysteresis behaviour were also observed (Figure 31f). The quality of the forward-scan data for the slowly cooled and 30 min samples is significantly worse than the other samples, and the J_{sc} values of the reverse scans for the same two samples are considerably lower than those of the 10- and 20-min samples. This behaviour can be explained by considering the oxygen doping, which increases the p-type character and work function of the perovskite samples that experience extended annealing. This could increase the downward band bending at the C₆₀/perovskite interface, raising the perovskite CB and thus creating a larger barrier at short circuit, which explains why the forward ($J_{sc} \rightarrow V_{oc}$) sweep shows lower J_{sc} and FF. In the reverse sweep ($V_{oc} \rightarrow J_{sc}$), the device starts at high bias, where interfacial dipoles have already formed and traps are filled, which partly relaxes the barrier and leads to improved current extraction.

A similar impact on current injection was observed when the device was operated under dark conditions. An increase in O-doping was found to reduce current injection at forward bias, as shown in Figure 10g.

Illumination-dependent current-density-voltage measurements were carried out on all samples (Figure A 5 in Appendix II). The ideality factor (n) quantifies how closely the device follows ideal diode behaviour and can be useful in identifying the dominant recombination mechanism under operation. When $n \approx 1$, recombination is thought to be band-to-band. When $n \approx 2$, trap-assisted recombination dominates. Values between 1 and 2 indicate mixed behaviour, and when $n > 2$ additional non-idealities such as series/shunt resistance or transport limitations are involved. The calculated n values for all the rapidly cooled samples are between 1.1 and 1.55, whilst the slowly cooled sample shows a significantly higher n of 2.4. Additionally, the dark saturation current density (J_0) seems to vary significantly between samples (Figure A 4 in Appendix II). The J_0 value of the slowly cooled device is clearly the highest, consistent with the sample being heavily O-doped and resulting in poor charge extraction.

Finally, Impedance spectra were collected for the same samples and fitted with a contact, transport, recombination, and Warburg model at 0 and 0.85 V. This equivalent-circuit framework separates small signal responses from the device into four distinct blocks, Figure 10h. In Figure 31i, the 20 mins device shows the lowest effective series resistance, consistent with its higher J_{sc} and FF. Similarly, this device condition shows the smallest recombination admittance (largest $R_{recombination}$), consistent with the higher V_{oc} , Figure 31i-j. The Warburg parameters indicate a weak and fast ionic response for the 20 mins sample (low Y_0 , ionic and B), whereas the 30 mins and slowly cooled devices exhibit stronger and/or slower ionic polarisation, matching the larger forward/reverse asymmetry. For the 10 mins device the transport resistance at 0 V is high and the ionic branch is weak but slow, which fits its lower FF and lower hysteresis observed in these devices. For the 30 mins device, transport is moderate, but the ionic term is strong and very slow, which explains the pronounced forward suppression. For the slowly cooled film, $R_{transport}$ is high, and the ionic response is strong with slow relaxation, consistent with good V_{oc} but larger hysteresis at short bias.

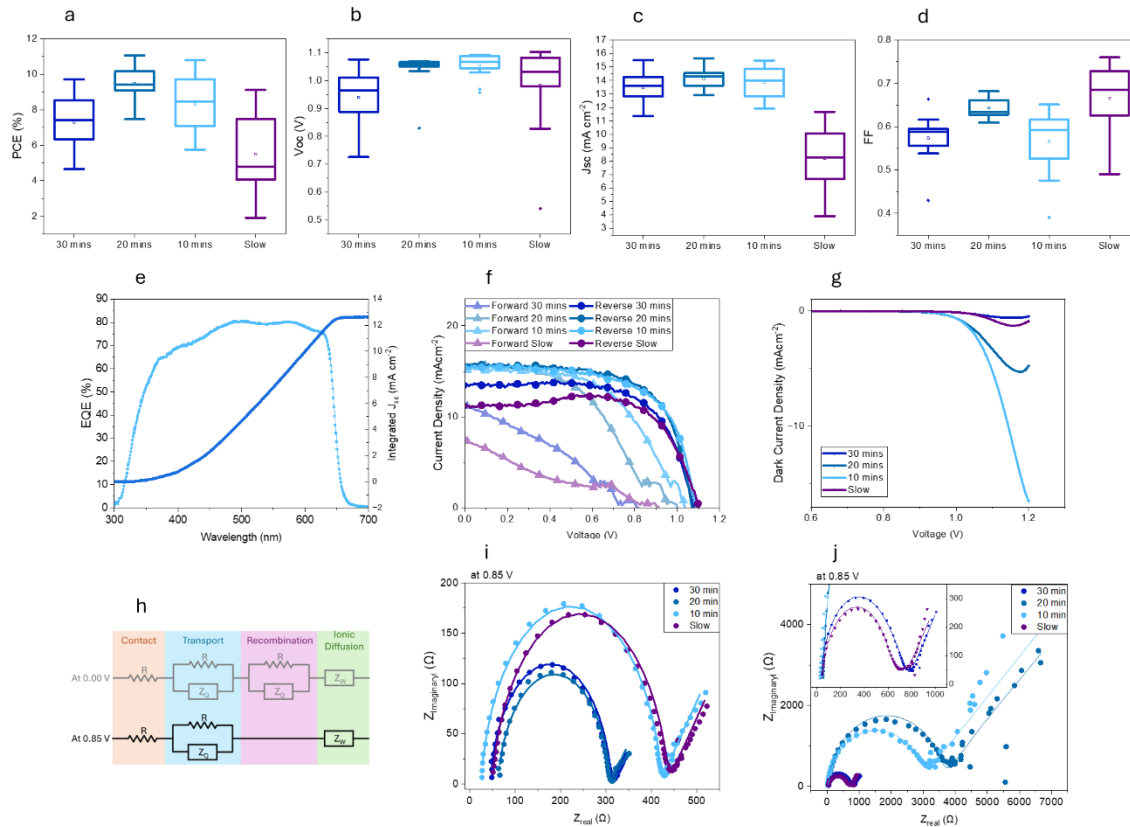


Figure 31- Device performance and electrical characterisation of CsPbI₂Br devices prepared under different cooling/annealing conditions. (a–d) Box plots of PCE, J_{sc} , V_{oc} , and FF for devices annealed for 10, 20, and 30 min with rapid cooling, and for slowly cooled films, showing optimum performance and reproducibility for the 20 min condition. (e) EQE spectrum of the champion 20 min device with integrated J_{sc} . (f) Forward and reverse $J-V$ curves highlighting hysteresis behaviour across processing conditions. (g) Dark $J-V$ curves showing differences in current injection and near- V_{oc}

behaviour. (h) Equivalent-circuit model used for EIS fitting. (i–j) Nyquist plots measured at 0.00 V and 0.85 V, respectively, showing reduced transport resistance and weaker ionic response for the 20 min device compared to the others.

5.12 Closing Remarks

This chapter introduces a reproducible processing methodology for all-inorganic CsPbI₂Br perovskite films for photovoltaic applications. A clear processing window was defined that combines solvent engineering, controlled warm-air exposure, and a slow post-annealing cool-down. Using this method, films with exceptional α -phase stability, enhanced photoluminescence, and improved morphological homogeneity were reproducibly prepared. Slow cooling in ambient air leads to unintentional oxygen incorporation, which shifts the conduction and valence band edges towards the vacuum level and induces p-type doping.

Varying the warm-air processing directly affects the homogeneity and uniformity of perovskite film coverage. Solvent variation shows a similar effect. The slow-cooling step is critical for the improved phase stability of the films. This improvement is likely caused by oxygen incorporation, changes in near-surface chemistry and electronic properties, local compositional variations near the surface, and the accumulation of strain in the films.

The optical quality of the films does not fully determine photovoltaic device performance. Device performance is mainly influenced by the intrinsic electronic properties of the films. These are affected by oxygen incorporation and its electronic effects, as well as structural changes near the surface.

When compared with the state-of-the-art, the devices fabricated here perform within the typical range of ambient-air-processed CsPbI₂Br solar cells. Our best-performing devices (20 min anneal) reached power conversion efficiencies of ~15 %. This value is comparable to ambient-air-processed CsPbI₂Br devices reported in the literature (typically 13-17 % PCE) and to glovebox-fabricated devices, which often achieve 14-17.5 % PCE^{130,175,176}. This suggests that our films achieve competitive bulk quality and that the remaining performance gap is primarily due to interfacial energetics rather than intrinsic film quality.

Oxygen should not be considered an unwanted or uncontrolled impurity. Instead, it can be used as a desirable dopant that, when deliberately and carefully incorporated, improves device performance. This work highlights the importance of controlling oxygen incorporation. It also shows the need to integrate these ambient-air-processed perovskite films with energetically well-aligned transport layers to take advantage of their improved stability and emission in next-generation perovskite photovoltaics and light-emitting devices.

Chapter 6: **Future Work and Outlook**

6.1 Pre-annealing of CsPbI₂Br

Industrial deployment of CsPbI₂Br perovskite solar cells has been hindered by poor reproducibility and uncontrolled crystallization, giving rise to voids, phase impurities, and device variability. In chapter 4, the impact of pre-annealing is investigated, demonstrating that introducing a controlled *low-temperature pre-annealing hold* at 15 °C stabilizes the intermediate phase and engenders uniform crystallization dynamics, which crucially are independent of the hold duration, a result not observed at higher pre-annealing temperatures. This finding provides a simple but impactful processing that could be easily incorporated into large-scale fabrication. Films processed with a 15 °C hold exhibit reproducible α -phase formation, reduced buried-interface voids, larger grain sizes, and superior optoelectronic quality; this in turn translates into higher power conversion efficiencies (PCEs) (~13 %) with enhanced fill factor (FF) and open-circuit voltage (V_{oc}) when compared with devices fabricated without this step .

In addition to improving the resultant morphology in the active layer of a solar cell, the 15 °C pre-annealing hold directly addresses a key persistent challenge in blade coating, where films remain wet for extended periods which gives rise to uncontrolled crystallization^{130,137,177}. Under conventional processing, long coating times promote premature nucleation, leading to heterogeneous phase formation and poor film uniformity. By holding the wet film at 15 °C, crystallization is slowed, and the intermediate phase is stabilized, preventing this uncontrolled growth . This ensures that the transition to the perovskite α -phase occurs uniformly only upon subsequent annealing, even when coating spans large areas or long-time windows. As a result, this holding step offers a practical route to suppress premature crystallization, minimize void formation, and deliver reproducible high-quality films in scalable bladding processes.

Introducing a low-temperature pre-annealing hold at 15 °C provides a simple yet powerful lever to improve the robustness of industrial CsPbI₂Br fabrication. Unlike conventional room-temperature holds, where crystallization accelerates unpredictably with time, the 15 °C condition sustains the intermediate phase regardless of hold duration. This decouples crystallization from the exact timing of subsequent annealing, eliminating one of the largest sources of variability in blade coating, where precise timing control is difficult to maintain across large substrates and multiple production lines^{120,178}. By ensuring uniform intermediate formation and suppressing void generation at the buried interface, the 15 °C hold step stabilizes film quality against fluctuations in operator handling, substrate loading, and line throughput. In practice, this transforms pre-annealing from a bottleneck into a tolerance-building step, making the overall process far more reproducible and compatible with scalable industrial manufacturing.

Although the buried-interface SEM analysis presented in Chapter 4 reveals a very clear and consistent trend in void formation as a function of hold time and temperature, a useful additional

verification in future work would be to image the substrate surface after the perovskite film has been peeled away during sample preparation. By examining whether any residual perovskite remains adhered to the substrate in regions corresponding to observed voids, it would be possible to conclusively rule out any contribution from the peeling process itself to the apparent void structure. This would serve as a confirmatory control, reinforcing that the observed interfacial voids originate from intrinsic crystallization dynamics during film formation rather than artefacts of sample preparation.

6.2 Air-processed CsPbI₂Br

In this work, we showed that warm-air-assisted slow cooling processing is an effective approach to produce bright and stable CsPb(I,Br)₃ films under ambient conditions. The films exhibit strong photoluminescence, improved structural uniformity, and long-lived α -phase stability compared to rapidly cooled controls. However, these improvements in film quality do not directly translate into higher device efficiencies. The main limitation arises from the unsatisfactory interfacial energetics, where poor alignment restricts efficient charge extraction. A key step in progressing this work further is therefore the development of interfacial engineering, which can be achieved through the doping of adjacent transport layers to encourage effective charge extraction at both the hole and electron transport layer interface.

While warm-air-assisted, slow-cooling processing significantly improves the intrinsic film quality of CsPb(I,Br)₃, the corresponding devices do not exhibit a proportional gain in photovoltaic performance. The central limitation lies in the interfacial energetics, which are strongly affected by oxygen incorporation during fabrication. As shown by APS and KP measurements, the slowly cooled films exhibit a reduced Fermi level to valence band offset ($E_F - E_{VBM} = 0.28$ eV) compared to rapidly cooled films (0.39 eV). This narrowing reflects stronger p-type doping at the surface, which we attribute to oxygen uptake during the extended annealing and cooling process. While such doping suppresses non-radiative recombination and enhances photoluminescence, it simultaneously shifts the energy levels, thus inhibiting charge extraction in our current architecture, emphasising the need for investigations into alternative CTLs.

This interfacial misalignment is directly reflected in the resulting device performance; Despite the slowly cooled films yielding the highest fill factors, their short-circuit current density (J_{sc}) and PCE are markedly reduced (Figure 6a-c). The forward-scan JV curves (Figure 6e) show suppressed current extraction near short-circuit conditions, consistent with increased downward band bending at the C60/perovskite interface due to the oxygen-driven surface doping. In contrast, the reverse scans are less affected, since interfacial dipoles and trap filling partially relax the extraction barrier under bias. The dark JV curves (Figure 6f) further confirm this behaviour, revealing hindered carrier injection consistent with elevated surface work function and poor interfacial selectivity.

Together, these observations indicate that the main bottleneck is not the quality of the bulk perovskite, which is excellent in slowly cooled films, but rather the oxygen-induced p-doping of the surface that shifts band alignment unfavourably. As a result, the strong photoluminescence and structural stability achieved through slow cooling cannot yet be fully translated into efficient device performance.

While ARXPS provided strong evidence of a vertical chemical gradient and surface-localised oxygen incorporation in these films, a valuable extension of this work would be to perform secondary ion mass spectrometry (SIMS) to obtain a fully quantitative elemental depth profile. Unlike ARXPS, which provides depth-weighted information averaged over the sampling volume, SIMS would enable direct measurement of oxygen, halide, and cation concentrations as a function of true film depth with nanometre-scale resolution. This would allow precise mapping of the extent of oxygen incorporation and compositional redistribution throughout the film thickness, providing definitive confirmation of the gradients inferred from ARXPS. Such data would directly strengthen the link between oxygen-induced surface doping, interfacial energetics, and the charge-extraction limitations observed in the p-i-n devices, thereby guiding the interfacial engineering strategies proposed below.

For the existing p-i-n architecture (ITO/MeO-2PACz / perovskite / C60 /BCP/Ag), the most immediate adjustment is to introduce an ultrathin dipole-forming interlayer between the perovskite and the electron-transport layer (ETL). n-type interlayers such as PFN-Br/PNDIT-F3N (conjugated polyelectrolytes) or PEIE/PEI (ultrathin, <5 nm) are well known to lower the adjacent work function and create an interfacial dipole that reduces the extraction barrier^{179–181}. In our case, these layers are expected to partially counteract the surface work-function rise seen by KP/APS (Figure 3a), thereby mitigating the forward-bias current suppression (Figure 6e) and improving J_{SC} without disturbing the bulk recombination landscape. As a fullerene-compatible alternative, amine-functional C60 (ICBA, or PCBM) can be used in place of neat C60 to embed the dipole within the ETL^{182,183}, while preserving the favourable transport and optical transparency of the fullerene contact. In all cases, the effectiveness should be verified *operando* by repeating the APS/KP sequence after each interlayer step and correlating the shifts with $Suns-V_{OC}$, illumination-dependent n (ideality) and near-SC impedance (to confirm that the fix targets extraction, not bulk recombination).

In the case that dipole tuning alone is insufficient, we propose to replace the ETL with materials that better tolerate or even benefit from the higher surface work function inferred from Figure 3a. Two practical substitutions for top-contact p-i-n are: (i) wide-gap n-layers like TPE-PDI₄¹⁸⁴ that present a deeper LUMO and strong interfacial dipole, and like NDI-C4F¹⁸⁵ (ii) inorganic ultrathin oxides deposited gently like low-temperature ALD SnO₂ and TiO₂^{186,187}. Both routes aim to lower the ETL vacuum level at the interface and reduce the barrier seen in forward scans (Figure 6e).

Beyond modifying the ETL, it is essential to perform a controlled comparison of p-i-n and n-i-p architectures under identical slow-cooling conditions. This experiment is critical to determine whether

the dominance of n-i-p in high-efficiency air-processed CsPbX₃ solar cells originates from interfacial energetics. A gradient p-type surface, as indicated by our APS/KP results, would be disadvantageous when interfaced with an ETL in the p-i-n configuration, but could yield favourable energetics when interfaced with an HTL in the n-i-p configuration. In this context, the internal field induced by the gradient band structure is expected to direct photogenerated holes toward the HTL while simultaneously driving electrons toward the ETL, thereby reinforcing charge separation in the n-i-p arrangement but partially opposing electron extraction in the p-i-n case.

Another promising direction for this work is in light-emitting diodes (LEDs). The strong and stable photoluminescence that we achieve through warm-air-assisted, slow-cooling processing makes these films highly attractive for electroluminescent devices. So far, most demonstrations of red all-inorganic perovskite LEDs have relied on nanocrystals or quantum dots, while reports using bulk 3D films remain very limited^{29,134,188–190}. This is largely due to the difficulty of producing phase-pure, emissive films with sufficient stability under ambient processing. Our results show that slow cooling can deliver bright and uniform CsPb(I,Br)₃ layers directly as 3D thin films, opening a pathway to LEDs without the need for colloidal synthesis or complex surface treatments. Exploring this route could therefore fill an important gap in the literature and establish a scalable route towards red perovskite LEDs with improved stability and reproducibility.

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Appendix I

This section details the script used in fitting XRD and GIXRD tracking studies.

```
function result = fit_expected_peaks(data, temperature, label_prefix, output_dir, all_peaks, search_windows)

% Inputs:
% data: [N x 2] array, columns = [2theta, intensity]
% temperature: scalar, used for labeling
% label_prefix: 'Rapidly' or 'Slow'
% output_dir: folder to save plots
% all_peaks: vector of target 2theta positions
% search_windows: vector of half-widths (in degrees) around each peak

x = data(:,1);
y = data(:,2);

% --- Background & smoothing ---
bg = polyfit([x(1:5); x(end-4:end)], [y(1:5); y(end-4:end)], 1);
y_corr = y - polyval(bg, x);
y_corr(y_corr < 0) = 0;
y_smooth = sgolayfilt(y_corr, 9, 35); % (order 9, frame 35)

% --- Results container ---
result = struct('Label', {}, 'Center', {}, 'Height', {}, ...
               'WidthL', {}, 'WidthR', {}, 'EtaL', {}, 'EtaR', {});
total_fit = zeros(size(x));

% --- Figure (headless for batch runs) ---
fig = figure('Visible','off');
subplot(2,1,1); hold on;
plot(x, y, 'k', 'DisplayName', 'Raw');
plot(x, y_smooth, 'b', 'DisplayName', 'Smoothed');
title(sprintf('%s %d °C', label_prefix, temperature));
xlabel('2theta (°)'); ylabel('Intensity');

% --- Fit each expected peak with asymmetric pseudo-Voigt ---
% Model parameters per peak: H, a, s1 (left width), s2 (right width), b1 (eta_L), b2 (eta_R)
model = fitype(@(H,a,s1,s2,b1,b2,x) ...
    (x<a).*H.*(b1./(1+((x-a)/s1).^2) + (1-b1).*exp(-log(2)*((x-a)/s1).^2)) + ...
    (x>=a).*H.*(b2./(1+((x-a)/s2).^2) + (1-b2).*exp(-log(2)*((x-a)/s2).^2)), ...
    'independent','x','coefficients',{'H','a','s1','s2','b1','b2'});

for i = 1:length(all_peaks)
    [x_fit, y_fit] = extract_peak_region(x, y_smooth, all_peaks(i), search_windows(i));
    if isempty(x_fit), continue; end

    % Initial guesses from local max
    [~, idx_max] = max(y_fit);
    a0 = x_fit(idx_max);
    H0 = y_fit(idx_max);
```

```

% Optional stabilizers for specific peaks (documented tweak)
if abs(all_peaks(i) - 29.5) < 0.05
    a0 = 29.5;
    H0 = H0 * 1.2;
end
if abs(all_peaks(i) - 30.3) < 0.05
    a0 = 30.3;
    H0 = H0 * 1.2;
end

% Bounds: keep widths modest; mixing factors in [0,1]
opts = fitoptions('Method','NonlinearLeastSquares', ...
    'StartPoint',[H0, a0, 0.1, 0.1, 0.5, 0.5], ...
    'Lower',    [0,  a0-0.2, 0.01, 0.01, 0,  0], ...
    'Upper',    [Inf, a0+0.2, 0.30, 0.30, 1,  1]);

try
    fitobj = fit(x_fit, y_fit, model, opts);
    y_model = feval(fitobj, x);
    total_fit = total_fit + y_model;

    plot(x, y_model, '--', 'LineWidth', 1.2, ...
        'DisplayName', sprintf('Fit @ %.1f°', all_peaks(i)));

    result(end+1) = struct( ...
        'Label', sprintf('%s %d P%.1f', label_prefix, temperature, all_peaks(i)), ...
        'Center', fitobj.a, ...
        'Height', fitobj.H, ...
        'WidthL', fitobj.s1, 'WidthR', fitobj.s2, ...
        'EtaL', fitobj.b1, 'EtaR', fitobj.b2);
catch
    % silently skip on failure
end
end

% Overlay total fit
plot(x, total_fit, 'm-', 'LineWidth', 2, 'DisplayName', 'Total Fit');
legend('Location','best');

% Residuals subplot
subplot(2,1,2);
residual = y_corr - total_fit;
plot(x, residual, 'r', 'DisplayName', 'Residual');
xlabel('2\theta (°)'); ylabel('Residual');
title('Fit Residual'); grid on;

% Save & close
saveas(fig, fullfile(output_dir, sprintf('%s_%d_fit.png', label_prefix, temperature)));
close(fig);
end

```

Appendix II

Table A 1- Reported photoluminescence Peak Positions of CsPbI₃, CsPbI₂Br, and CsPbIBr₂ Perovskite Films.

Composition	PL Emission (nm)	Reference (ACS Style)
CsPbI ₃	700.6 (~1.77 eV)	Yi, C.; Luo, J.; Meloni, S.; Boziki, A.; Ashari-Astani, N.; Gratzel, C.; Zakeeruddin, S. M.; Rothlisberger, U.; Gratzel, M. <i>Nat. Commun.</i> 2020, 11, 2278. https://doi.org/10.1038/s41467-020-15639-x
CsPbI ₃	700	Wu, Z.; Chen, W.; Zhang, J.; et al. <i>Opt. Express</i> 2020, 28 (15), 21805-21814. https://doi.org/10.1364/OE.28.021805
CsPbI ₃	697-706	Gao, F.; Zhao, X.; Li, J.; et al. <i>Adv. Energy Sustain. Res.</i> 2022, 3 (7), 2200015. https://doi.org/10.1002/aesr.202200015
CsPbI ₂ Br	652-659	Fan, Q.; Meng, F.; Ma, Q.; et al. <i>Joule</i> 2019, 3 (2), 372-386. https://doi.org/10.1016/j.joule.2018.10.011
CsPbI ₂ Br	653	He, Z.; Xu, Z.; et al. <i>RSC Adv.</i> 2019, 9, 31168-31174. https://doi.org/10.1039/C9RA06621A
CsPbIBr ₂	610	Stewart, R.; Lee, T.; et al. <i>J. Mater. Sci.</i> 2021, 56, 13410-13421. https://doi.org/10.1007/s10853-021-06552-3
CsPbIBr ₂	585	Xu, Z.; Zhang, X.; et al. <i>Physica B</i> 2024, 665, 415004. https://doi.org/10.1016/j.physb.2023.415004
CsPbIBr ₂	598-607	Zhang, H.; Wang, Y.; et al. <i>Energy Technol.</i> 2022, 10 (5), 2101285. https://doi.org/10.1002/ente.202101285
CsPbBr ₃	525	Chen, J.; Dong, H.; et al. <i>J. Am. Chem. Soc.</i> 2017, 139 (40), 13525-13532. https://doi.org/10.1021/jacs.7b07719
CsPbBr ₃	525	Yan, Y.; et al. <i>Opt. Express</i> 2020, 28 (9), 13484-13493. https://doi.org/10.1364/OE.386237
CsPbBr ₃	520	Bai, S.; Yuan, Z.; et al. <i>ACS Omega</i> 2022, 7 (3), 2584-2592. https://doi.org/10.1021/acsomega.1c05938

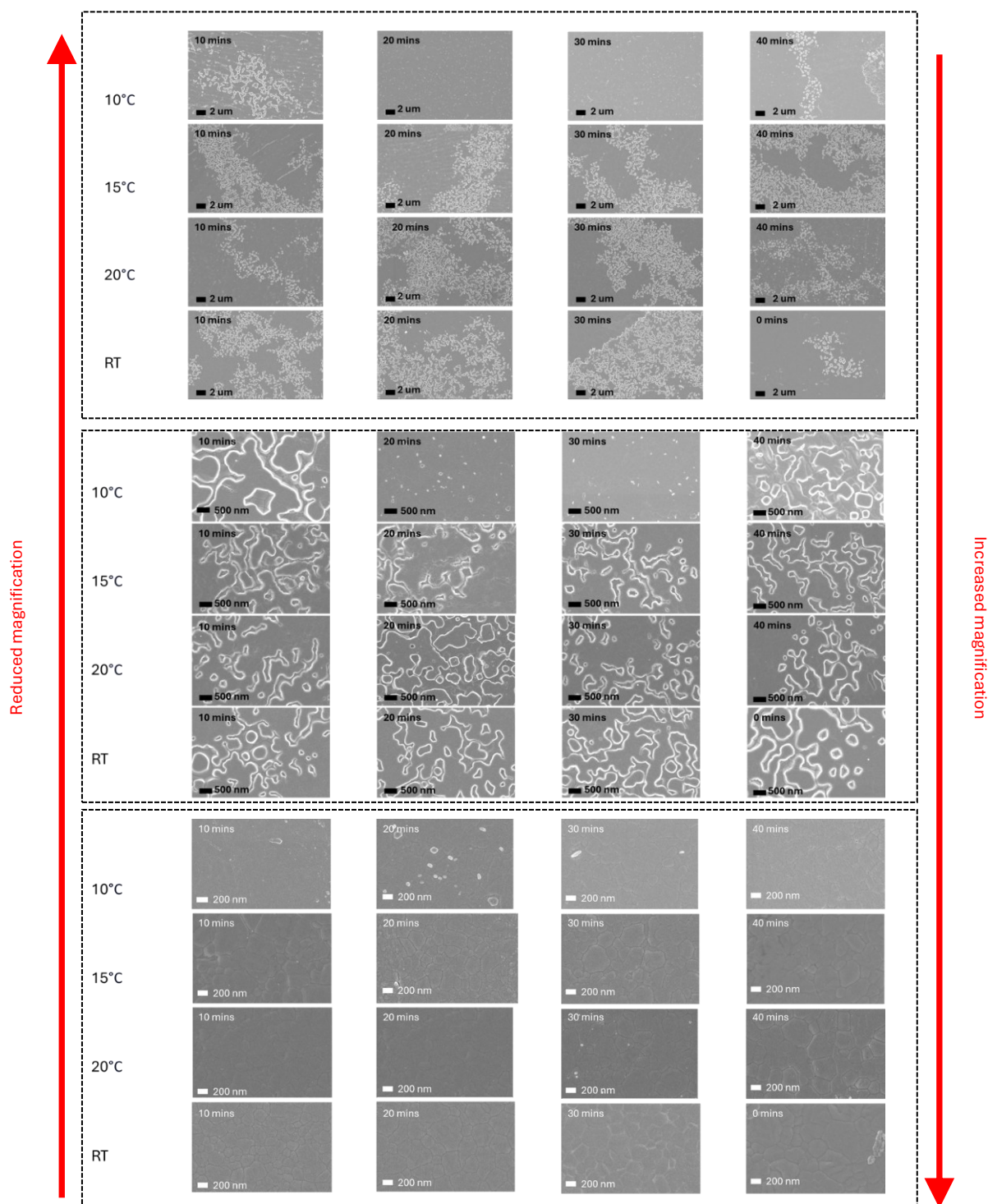


Figure A 1 - Buried-interface SEM as a function of hold duration and hold temperature at multiple magnifications. Columns show films held for 10, 20, 30, and 40 min; rows correspond to the indicated hold temperatures. Magnification increases from top to bottom (2 μm, 500 nm, and 200 nm scale bars), as shown.

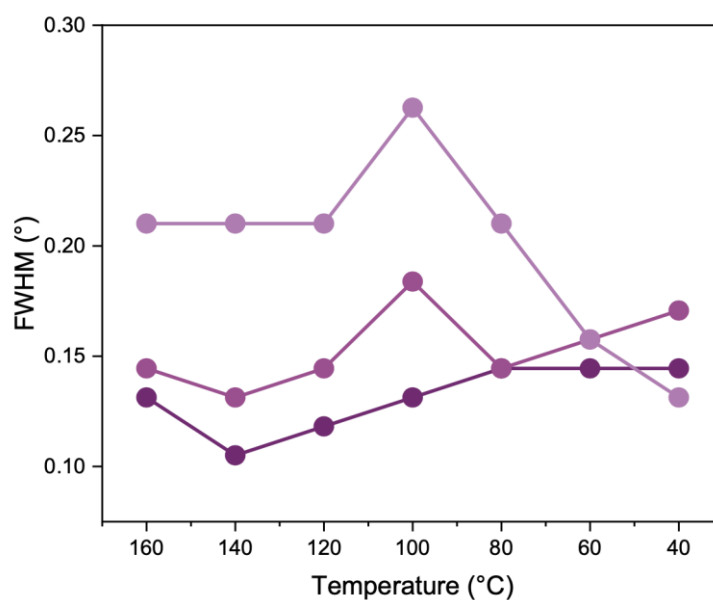


Figure A 2 - FWHM of in situ XRD analysis of CsPbI₂Br films during slow cooling (5 °C min⁻¹) from 160 °C to 40 °C.

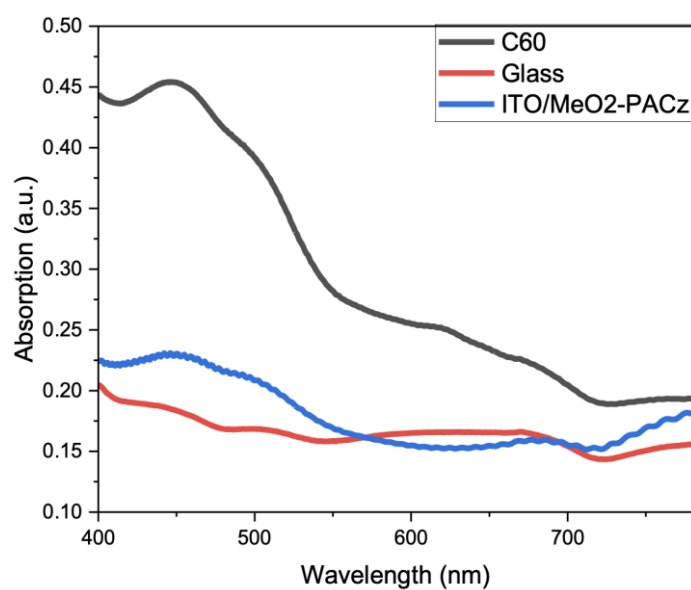


Figure A 3 - Optical absorption of layers used in PL geometry: C₆₀, glass, and ITO/MeO-2PACz, highlighting the C₆₀ absorption edge near ~670 nm.

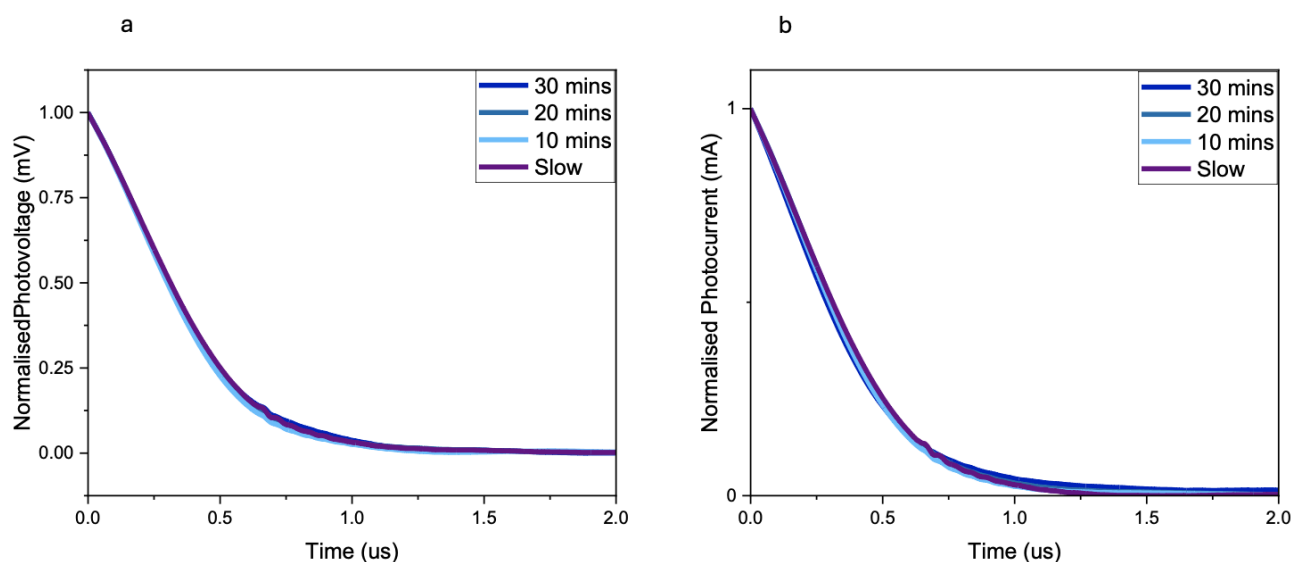


Figure A 4 - (a) TPV and (b) TPC of films fabricated with warm-air: 30 mins, 20 mins, 10 mins rapidly cooled samples, and slowly cooled sample

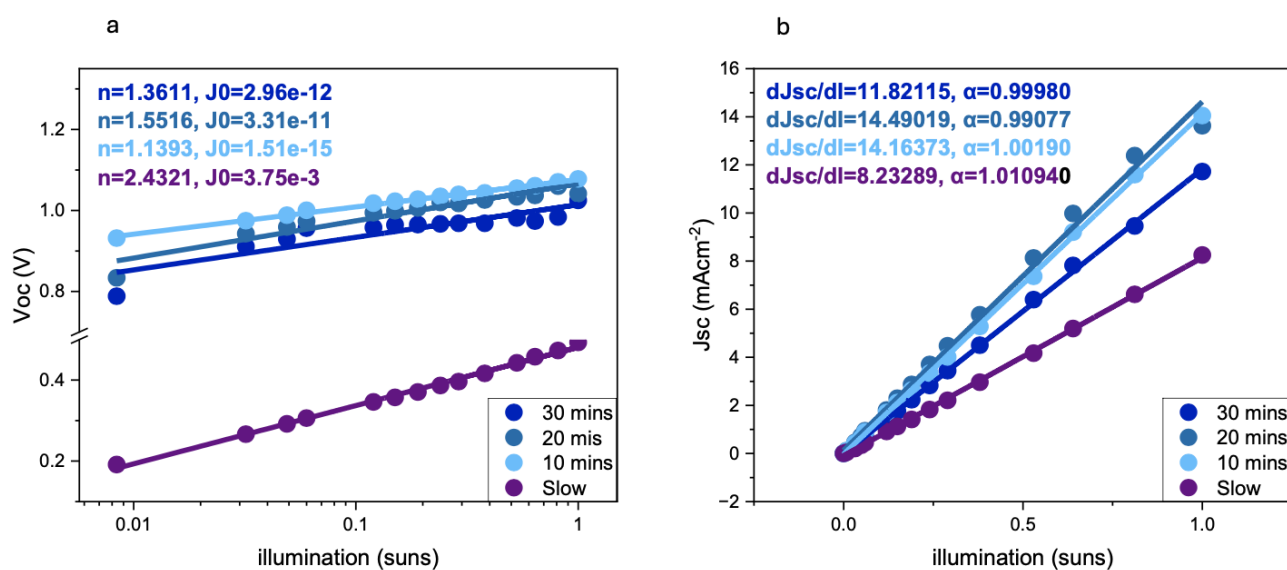


Figure A 5 - illumination-dependent (a) V_{oc} and (b) J_{sc} measurement of films fabricated with warm-air: 30 mins, 20 mins, 10 mins rapidly cooled samples, and slowly cooled sample