
**Circumventing the Miscibility Gap:
Kinetic Pathways to Ensure True
Bandgap Tunability in Metal Halide
Perovskites**



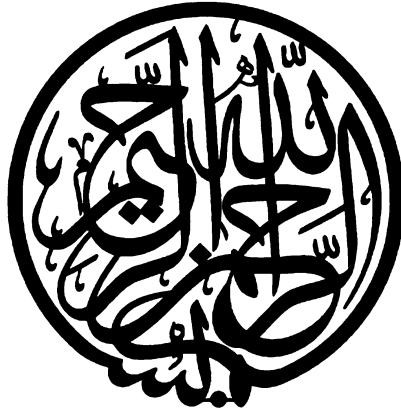
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For my father, whose name I carry. For my mother, whose smile I carry.



Two roads diverged in a wood, and I-
I took the one less travelled by,
And that has made all the difference.

- Robert Frost

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ABSTRACT

Mixed-halide metal halide perovskites offer tunable bandgaps and are promising candidates for photovoltaic applications. However, the practical use of formamidinium (FA)-based mixed-halide perovskites has been limited by the presence of a compositional miscibility gap, which prevents the formation of the photoactive α -phase across a significant portion of the iodide–bromide composition range using conventional processing methods.

In this work, the miscibility gap is reproduced experimentally and its origin is investigated using machine-learning interatomic potential (MLIP) modelling. The results show that the miscibility gap arises from a near-degeneracy in the Gibbs free energy of the α - and δ -phases at intermediate bromide compositions, rather than from an intrinsic instability of the α -phase alone. The results also indicate that the presence of the miscibility gap, and the degree of suppression of the α -phase, are dependent on the crystallisation pathway used to process the films.

Based on this, a 2D/3D templated crystallisation strategy is developed using butylammonium-based Ruddlesden–Popper templates. This approach enables phase-pure α -FAPb(I_{1-x}Br_x)₃ to be obtained across the full composition range. Computational modelling suggests that the 2D template stabilises mixed-halide compositions through site-selective ordering on inequivalent halide sites, while subsequent thermal conversion kinetically preserves the halide framework. The resulting films exhibit favourable optoelectronic properties, including high charge-carrier mobility and long carrier lifetimes. Photovoltaic devices fabricated using the templated films achieve a

stabilised power conversion efficiency of 17.1%, demonstrating the viability of this approach for device applications.

The final set of investigations examined whether Cs incorporation or templating plays a more important role in determining film stability. Although Cs was successfully incorporated into the films, they remained metastable and were substantially less stable than conventional FACs films. As a result, this question remains unresolved, as the templated films exhibit a distinct degradation pathway that appears to be independent of Cs content.

Overall, this work provides both a comprehensive understanding of the miscibility gap and a practical strategy for overcoming it, enabling access to FA-based mixed-halide perovskites across the full compositional space.

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INTRODUCTION

1.1 GLOBAL ENERGY DEMAND

Over the past two centuries, society has undergone unprecedented socio-economic transformation. While multiple factors have contributed to this change, it is closely associated with the post-industrial technological revolution. Modern societies are increasingly defined by the technologies they produce and the energy required to sustain them. Advances such as modern medicine, transportation systems, entertainment, and climate control all depend on the large-scale manipulation of energy.

As the benefits of these technologies have become more apparent in developed economies, there has been a growing effort to extend access to them globally. This drive towards greater technological accessibility and ubiquity has contributed to a sustained rise in energy demand. Historically, improvements in the efficiency of various technologies might have been expected to limit the growth in energy consumption caused by mass technological adoption. Indeed, global energy consumption increased at a relatively moderate rate of approximately 1–2% per year.¹ However, in recent years, this rate has accelerated, driven in part by emerging technologies such as artificial intelligence. These technologies are particularly energy-intensive, with data centre electricity demand projected to grow several times faster than overall electricity demand.²

A central issue arising from increasing energy demand is the continued reliance on fossil fuels. The environmental consequences of fossil fuel use are well established, particularly their role in driving climate change.³ As global temperatures continue to rise, the impacts are expected to extend across multiple aspects of society, including economic stability, public health, and infrastructure. If current warming trends persist, these pressures are likely to intensify, placing systemic stress on both natural and human systems.⁴

1.2 RENEWABLE ENERGY

In order to meet increasing energy demands without compounding environmental damage, the transition to more sustainable methods of energy production has received growing attention. This shift aligns with a broader emphasis on sustainability, defined as the ability to maintain the long-term health of a system while continuing to support development. The United Nations defines sustainable development as meeting "the needs of the present without compromising the ability of future generations to meet their own."⁵ Consequently, the expansion of renewable energy technologies has become central to achieving a more sustainable model of progress.

Renewable energy encompasses a range of energy sources, including wind, solar, geothermal, and tidal power. What unites these sources is that they rely on naturally replenishing resources, in contrast to fossil fuels, which are finite on human timescales. Solar energy gives rise to many other energy sources by driving fundamental Earth system processes. Through photosynthesis, plants convert solar radiation into chemical energy, which is stored in biomass and, over geological timescales, forms fossil fuels such as coal, oil, and natural gas⁶. Uneven solar heating of the Earth's surface creates atmospheric pressure differences that generate wind, making wind energy an indirect form of solar power⁷. Similarly, solar radiation drives the hydrological cycle by causing evaporation, cloud formation, and precipitation, thereby enabling hydropower through the movement of water at elevated positions⁸.

As a result, a significant proportion of the Earth's usable energy resources can be traced back to solar radiation as their primary origin. Furthermore, the scale of this resource is immense: the amount of solar energy reaching the Earth's surface in approximately one hour exceeds total annual global energy consumption.⁹ Despite this abundance, the ability to efficiently capture, convert, and store solar energy remains a key limiting factor.

1.3 PHOTOVOLTAIC TECHNOLOGY

One method of utilising the energy available in the solar spectrum is through photovoltaic technology. Photovoltaics currently produce around 7% of global electricity, up from just 0.1% in 2010.³ It is now the fastest-growing source of electricity, with its share doubling in recent years and expected to continue rising rapidly.¹⁰ The rapid expansion of solar energy has been largely enabled by advances in silicon photovoltaic technology, which dominates the market due to its low cost, improving efficiency, scalability, and long operational lifespan. Crystalline silicon technologies account for approximately 95% of currently deployed solar panels.¹⁰ The cost of manufacturing has fallen by nearly 90% since 2010, making solar increasingly competitive with conventional energy sources. In many regions, solar electricity is now the cheapest form of new power generation, even compared to fossil fuels.¹¹

However, while silicon technologies have made a significant contribution to renewable energy deployment, there remains scope for further reduction in the levelised cost of electricity (LCOE). One approach to reducing costs further is to increase the efficiency of solar modules without significantly increasing manufacturing costs or compromising stability.

Considering single-junction silicon cells as an example, these have a bandgap of approximately 1.12 eV. This means their theoretical maximum efficiency is limited to around 32% under the detailed-balance limit.¹² Tandem solar cells represent a promising pathway for surpassing the single-junction detailed-balance limit. These devices combine two or more photovoltaic materials with different bandgaps to harness a greater portion of the solar spectrum than is possible with single-junction cells.¹³ In principle, an infinite-junction tandem can achieve efficiencies of up to 68%, although practical devices typically employ 2–4 junctions. In a tandem cell each junction must have carefully selected bandgaps to maximise overall energy conversion efficiency.¹³

Since silicon does not possess a tunable bandgap, alternative materials must be explored for tandem applications. Metal halide perovskites are particularly well suited for this purpose because their bandgaps can be tuned through compositional engineering, enabling efficient integration

with silicon and other absorbers.¹⁴ Perovskite solar cells (PSCs) have rapidly emerged as a leading candidate among next-generation photovoltaic technologies. PSCs utilise low-cost, solution-processable metal halide perovskite semiconductors as their absorber layer.^{15,16} They combine several key advantages, including high efficiency, low-temperature processing, and compatibility with scalable manufacturing techniques.¹⁴ In recent years, perovskites have attracted significant attention due to their rapid improvement in performance, with single-junction efficiencies reaching 27.3%, approaching those of laboratory-scale silicon devices.¹⁷

Currently, the record efficiency for single-junction silicon cells is approximately 27.9%. In contrast, state-of-the-art perovskite-silicon tandem solar cells have reached efficiencies of approximately 35.0%¹⁷, with recent reported values reaching 36.1%. Single-junction silicon cells have a theoretical efficiency limit of approximately 33%, whereas two-terminal silicon–perovskite tandems have a theoretical limit approaching 42%.^{12,13} This highlights the significantly greater potential for efficiency improvements offered by tandem technologies compared to single-junction silicon devices.

1.3 THESIS OVERVIEW

This thesis aims to develop an understanding of the limitations in bandgap tunability in metal halide perovskites for specific compositions. Chapter 2 introduces the fundamental physics required to understand the work presented in this thesis. Chapter 3 outlines the experimental methods used to investigate the properties of the materials studied in the experimental chapters. Chapter 4 examines the origin of the miscibility gap and how it depends on different crystallisation pathways. Chapter 5 presents a novel processing method that eliminates the miscibility gap, characterises the optoelectronic properties of these materials, and demonstrates their integration into photovoltaic devices. Chapter 6 applies this processing method to investigate the stability of metal halide perovskites under photothermal stress, addressing whether composition or processing has a greater influence on stability.

Ultimately, this thesis develops a comprehensive framework for understanding the formation of photoactive perovskite phases within competitive energetic landscapes and develops novel processing strategies that allow, for the first time, the formation of pure formamidinium (FA)-based mixed-halide perovskites.

THEORETICAL BACKGROUND

This section outlines the fundamental physical concepts necessary for understanding the work presented in this thesis. It focuses on the physics of semiconductor materials relevant to photovoltaic applications, with particular emphasis on the properties of perovskite materials that make them especially suitable for use in solar cells.

2.1 PHYSICS OF SEMICONDUCTORS

This section is heavily derived from "The Oxford Solid State Basics" and the Condensed Matter Physics course taught by Steve Simon.¹⁸ The sections about the operation of solar cells is based on "The Physics of Solar Cells" written by Jenny Nelson.¹⁹

Semiconductors

One way to classify materials is based on their electronic properties. At the most general level, materials can be categorised as metals, insulators, or semiconductors. The key factor determining this classification is the band structure, specifically the size of the bandgap. In metals, there is an overlap between the highest occupied electronic band (the valence band) and the lowest unoccupied band (the conduction band). As a result, electrical conduction can occur even at 0 K, since electrons can occupy the conduction band without requiring thermal excitation.

In contrast, insulators and semiconductors possess an energy gap (bandgap) between the valence and conduction bands. At 0 K, these materials do not conduct electricity, as electrons remain confined to the valence band. However, at finite temperatures, thermal excitation can promote electrons across the bandgap into the conduction band. The distinction between insulators and semiconductors is determined by the ease of thermally exciting charge carriers across this gap.

The fraction of electrons in the conduction band in both semiconductors and insulators is governed by an exponential factor, $\sim e^{-E_g/2kT}$, making it extremely sensitive to the bandgap E_g . In semiconductors, where E_g is relatively small (on the order of 0.1 eV to 3 eV), this fraction is small but still significant (for example, around 10^{-9} at room temperature), allowing measurable electrical conduction. In contrast, insulators typically have much larger bandgaps (greater than 4 eV), leading to an exponentially smaller fraction (for example, 10^{-40} or less), so virtually no electrons are thermally excited into the conduction band. Thus, although both classes of materials contain very few conducting electrons at room temperature, semiconductors possess enough to

conduct, whereas insulators effectively do not. To understand the properties of semiconductors in greater detail, it is necessary to introduce band theory more rigorously.

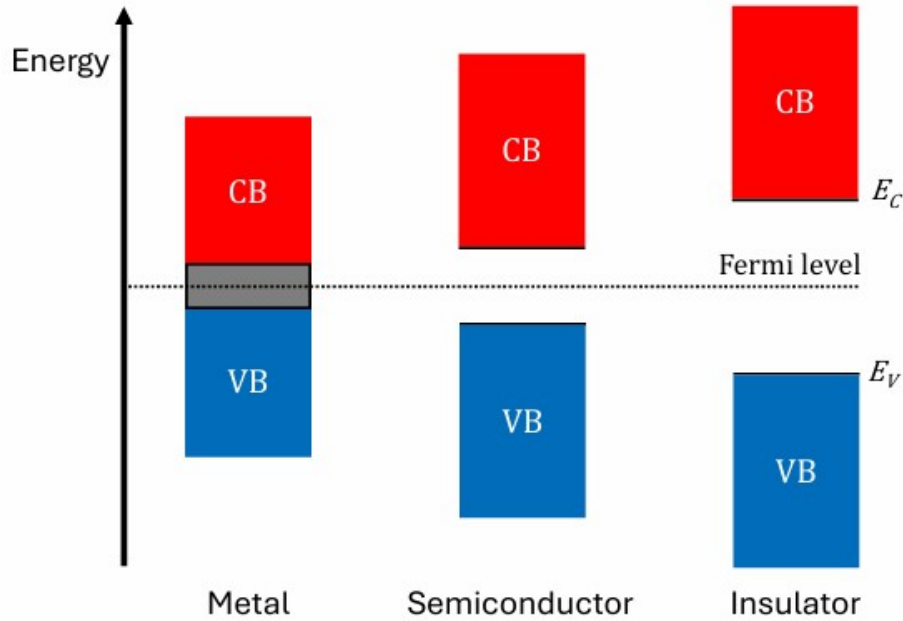


Figure 2.1: Energy-band diagram for an insulator, a semiconductor and a metal. The vertical extent of the boxes indicates the allowed energy regions. For the insulator, these are separated by a large bandgap ($E_g > 4$ eV), for the semiconductor the bandgap is smaller ($E_g = 0.1$ eV to 3 eV), and for the metal the two regions overlap, there is no bandgap.²⁰

2.1.1 Band Theory

The potential landscape in the bulk of a solid material is an emergent property of the bonding between the constituent elements and their orbitals. This is why reciprocal space (k -space) is a useful framework for analysing these systems, as it provides the set of allowed wavevectors that an electron can occupy and directly relates these to the electron energy. This relationship is commonly referred to as the dispersion relation.

In the case of a free (unbound) electron in a solid, the dispersion relation is given by:

$$E(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad (2.1)$$

where $\hbar$ is the reduced Planck constant, m is the electron mass, and k is the wavevector. The corresponding wavefunction describing the propagation of the electron is:

$$\Psi = Ae^{i(\mathbf{k} \cdot \mathbf{r})} \quad (2.2)$$

where A is a constant and $\mathbf{r}$ is the position vector.

When extending from the free-electron case to an electron in a periodic lattice (and hence a periodic potential), Bloch's theorem is invoked. This states that the wavefunction can be written as the product of a plane wave and a function with the periodicity of the lattice. For a Hamiltonian of the form

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}), \quad \text{where } V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}), \quad (2.3)$$

there exist solutions of the form

$$\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \Phi_{\mathbf{k}}(\mathbf{r}), \quad (2.4)$$

where $\Phi_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice. This periodicity can be expressed as

$$\Phi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \Phi_{\mathbf{k}}(\mathbf{r}), \quad (2.5)$$

for any lattice vector $\mathbf{R}$.

The specific form of $\Phi_{\mathbf{k}}(\mathbf{r})$ depends on the approximation used to describe the lattice potential. The periodic nature of the lattice allows the allowed values of $\mathbf{k}$ to be restricted to the first Brillouin zone (BZ), defined in one dimension as $-\pi/a \leq k \leq \pi/a$. The resulting dispersion relations are known as band structures, consisting of allowed energy bands separated by forbidden energy gaps. This is illustrated in Figure 2.2.

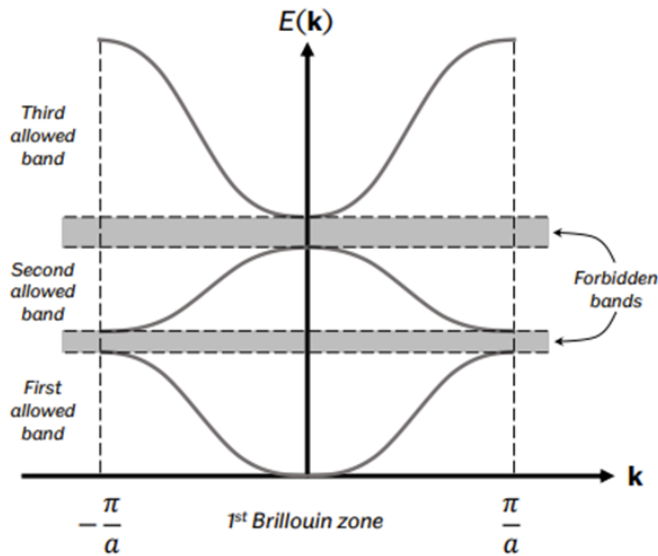


Figure 2.2: The first Brillouin zone, showing electron bands confined to $-\pi/a \leq k \leq \pi/a$, along with forbidden energy regions where electron states do not exist.

The shape of the dispersion relation can be understood by applying perturbation theory to the free-electron states in the presence of a periodic potential. Energy gaps emerge at the Brillouin zone boundaries due to the mixing of electron wavefunctions with degenerate wavevectors. This interaction splits the energy levels, lowering some states and raising others, thereby creating forbidden energy regions.

Whether a bandgap exists between neighbouring bands depends on the nature of the lattice potential and the degree of electron localisation. In metals, significant band overlap occurs due to delocalised electrons, enabling free conduction. In contrast, semiconductors and insulators exhibit bandgaps due to greater localisation of electronic states. As discussed previously, the magnitude of the bandgap largely determines whether a material behaves as a semiconductor or an insulator.

2.1.2 Charge Carrier Properties

The behaviour of electrons in a crystalline material can be understood from its band structure. When an electron gains sufficient energy, it can be promoted from the valence band into the conduction band, leaving behind a vacant state referred to as a hole. Typically, this excitation occurs from the valence band maximum (VBM) to the conduction band minimum (CBM). The nature of this transition depends on the relative positions of these extrema in momentum ($\mathbf{k}$) space. If the VBM and CBM are located at the same $\mathbf{k}$ -vector, the transition can occur solely through photon absorption once the photon energy exceeds the band gap; this is termed a direct transition. In contrast, if the VBM and CBM lie at different points in $\mathbf{k}$ -space, conservation of crystal momentum requires the involvement of a phonon in addition to the photon. Such a process is referred to as an indirect transition.

Electrons and holes are charge carriers, and their concentration in a material depends strongly on both temperature and band gap. In an intrinsic material, the carrier population is determined by the number of electrons thermally excited into the conduction band at a given temperature T . Evaluating this concentration requires consideration of two factors: the probability that an energy state is occupied and the number of available states at that energy.

The occupation probability of a state with energy ε is described by the Fermi–Dirac distribution:

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - E_F}{k_B T}\right) + 1}, \quad (2.6)$$

where E_F is referred to as the Fermi level. This function gives the probability that a state at energy ε is occupied by an electron under thermal equilibrium. The Fermi level corresponds to the energy at which the occupation probability is $1/2$.

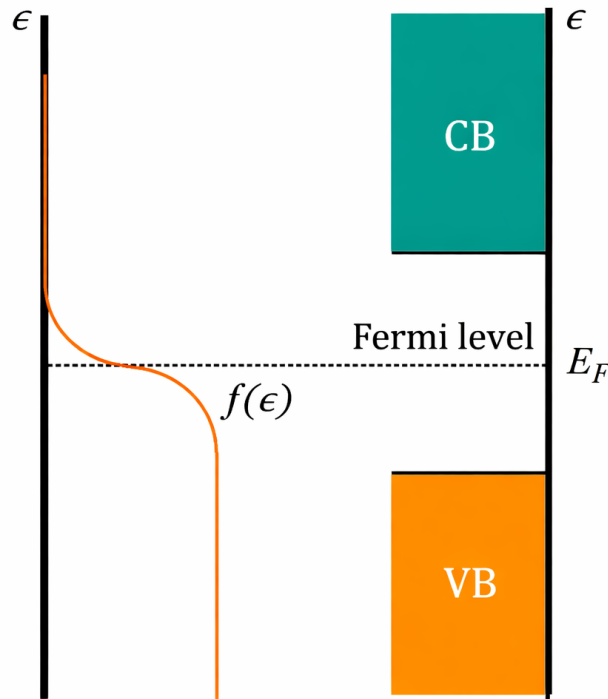


Figure 2.3: The Fermi–Dirac distribution and corresponding band structure on the same energy scale for an intrinsic semiconductor, showing that the occupation probability is $\frac{1}{2}$ at the fermi-level.

To determine the electron concentration in the conduction band and the hole concentration in the valence band, the density of states (DOS) must also be considered. The DOS, defined as the number of available states per unit energy per unit volume, depends on energy and arises from the quantised solutions of the Schrodinger equation. Importantly, the form of the DOS is strongly dependent on the dimensionality of the system, leading to significant differences between bulk and low-dimensional materials.

2.1.3 Absorption, Generation and Recombination

Some semiconductors such as silicon possess optoelectronic properties that are well suited for photovoltaic applications. Photovoltaic materials absorb photons and convert their energy into electricity. Provided that a photon has energy at least equal to the bandgap of the material, it can generate an electron-hole pair. Silicon has a bandgap of 1.1 eV; therefore, only light with wavelengths shorter than 1127 nm can excite electrons in silicon. Any excess energy is transferred to the charge carriers as kinetic energy, which is rapidly lost as heat as electrons and holes thermalise to the band edges on femtosecond timescales.

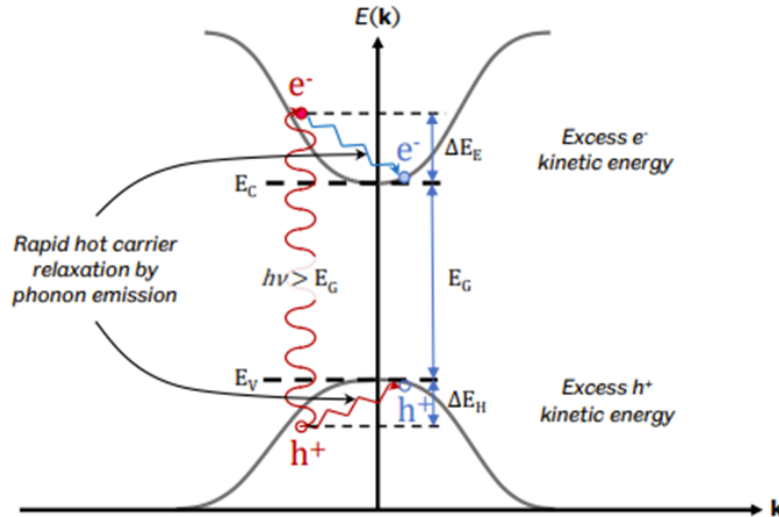


Figure 2.4: Energy level diagram illustrating the absorption of a photon with energy greater than the material bandgap. An electron is promoted to the conduction band, leaving a hole in the valence band. Carriers relax to the band edges, releasing the excess energy.

Following photon absorption, an electron-hole pair is generated. If the material exhibits effective charge screening, the exciton can dissociate into free charge carriers. These carriers can then undergo several processes. Radiative recombination results in the emission of a photon with energy approximately equal to the bandgap. Alternatively, non-radiative recombination may occur via trap states or at interfaces. In such cases, energy is dissipated without photon emission, or photons of lower energy may be emitted if recombination occurs through states within the bandgap.

2.1.4 Nonequilibrium Carrier Populations under Photogeneration

An important consequence of photogeneration in semiconductors is the deviation from thermal equilibrium due to external perturbations. Upon exposure to light or an applied electric bias, the populations of electrons and holes increase beyond their equilibrium values and can no longer be described by a single Fermi-Dirac distribution.

Under nonequilibrium conditions, electrons in the conduction band and holes in the valence band are described by separate distribution functions, $f_c(\mathbf{k}, \mathbf{r})$ and $f_v(\mathbf{k}, \mathbf{r})$, which depend on both position and wavevector. A key simplification, valid when the perturbation is neither too strong nor too rapid, is that the electron and hole populations can each reach a quasi-thermal equilibrium. In this case, their distributions may be approximated by

$$f_c(\mathbf{k}, \mathbf{r}) \approx f_0(E, E_{F_n}, T_n) \quad (2.7)$$

$$f_v(\mathbf{k}, \mathbf{r}) \approx f_0(E, E_{F_p}, T_p) \quad (2.8)$$

where E_{F_n} and E_{F_p} are the electron and hole quasi-Fermi levels, and T_n and T_p are the effective carrier temperatures.

The electron and hole densities under quasi-thermal equilibrium are given by

$$n = n_i \exp\left(\frac{E_{F_n} - E_i}{k_B T_n}\right) \quad (2.9)$$

$$p = n_i \exp\left(\frac{E_i - E_{F_p}}{k_B T_p}\right) \quad (2.10)$$

where n_i is the intrinsic carrier concentration and E_i is the intrinsic energy level. Since photo-generated carriers rapidly thermalise with the lattice, it is typically assumed that $T_n = T_p = T$. Because $E_{F_n} \neq E_{F_p} \neq E_F$, the separation between the quasi-Fermi levels is defined as the *quasi-Fermi level splitting*

$$\Delta\mu = E_{F_n} - E_{F_p}. \quad (2.11)$$

The electron-hole product under nonequilibrium conditions becomes

$$np = n_i^2 \exp\left(\frac{\Delta\mu}{k_B T}\right). \quad (2.12)$$

This is called the law of mass action and is invariant for small amounts of doping.

2.1.5 Charge Separation

To generate electrical power via the photovoltaic effect, photogenerated electrons and holes must be separated and collected. This requires an asymmetric structure, most commonly a semiconductor p-n junction.

Starting from the Boltzmann transport equation under the relaxation-time approximation, the electron and hole current densities are given by

$$\mathbf{J}_n(\mathbf{r}) = \mu_n n \nabla E_{F_n} \quad (2.13)$$

$$\mathbf{J}_p(\mathbf{r}) = \mu_p p \nabla E_{F_p}, \quad (2.14)$$

where μ_n and μ_p are the electron and hole mobilities. The total current density is $\mathbf{J} = \mathbf{J}_n + \mathbf{J}_p$. Thus, photovoltaic energy conversion requires illumination to generate a spatial gradient in at least one of the quasi-Fermi levels. Carrier transport can be described using the drift-diffusion model. Drift currents arise from electric fields, while diffusion currents originate from carrier concentration gradients. The drift components are

$$\mathbf{J}_n^{\text{drift}} = \mu_n n \mathbf{E} = -\mu_n n \nabla \phi \quad (2.15)$$

$$\mathbf{J}_p^{\text{drift}} = \mu_p p \mathbf{E} = -\mu_p p \nabla \phi, \quad (2.16)$$

where ϕ is the electrostatic potential. The diffusion components are

$$\mathbf{J}_n^{\text{diff}} = q D_n \nabla n \quad (2.17)$$

$$\mathbf{J}_p^{\text{diff}} = -q D_p \nabla p, \quad (2.18)$$

with D_n and D_p denoting the diffusion coefficients.

In one dimension, the total current densities become

$$J_{nT} = -q\mu_n n \frac{d\phi}{dx} + qD_n \frac{dn}{dx} \quad (2.19)$$

$$J_{pT} = -q\mu_p p \frac{d\phi}{dx} - qD_p \frac{dp}{dx}. \quad (2.20)$$

2.1.6 Formation of the p-n Junction

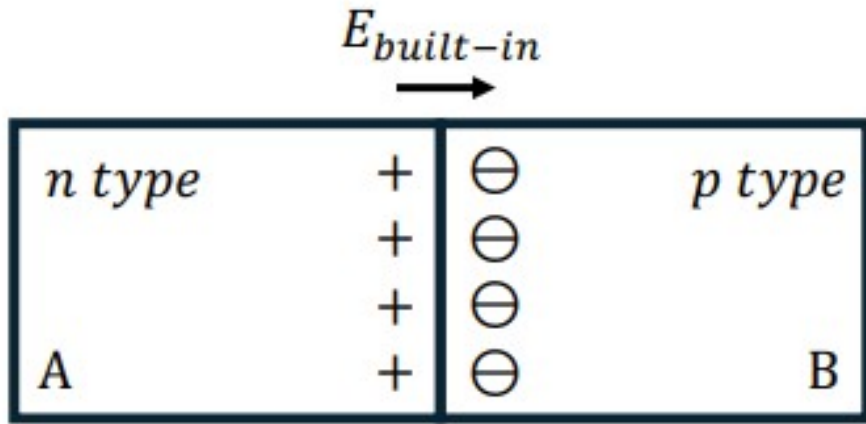


Figure 2.5: Block A and Block B are n-type and p-type semiconductors, respectively. The diagram shows the built-in electric field that arises, pointing from Block A to Block B, when the two blocks are in contact.

Consider two semiconductor regions: an n-type region (Block A) and a p-type region (Block B). When these regions are brought into contact, electrons diffuse from the n-type region into the p-type region, leaving behind positively charged donor ions near the interface. Simultaneously, negatively charged acceptor ions accumulate on the p-type side.

This space charge creates an internal electric field directed from the n-type to the p-type region, known as the built-in electric field. The field generates a drift current that counteracts diffusion, resulting in zero net current at equilibrium. The region depleted of mobile carriers is referred to as the depletion region. When isolated, the two materials have independent Fermi levels. Upon contact, the Fermi levels align, leading to band bending. The built-in potential is given by

$$V_{bi} = \frac{1}{q}(\phi_A - \phi_B). \quad (2.21)$$

Where ϕ_A and ϕ_B are the work functions of the two materials.

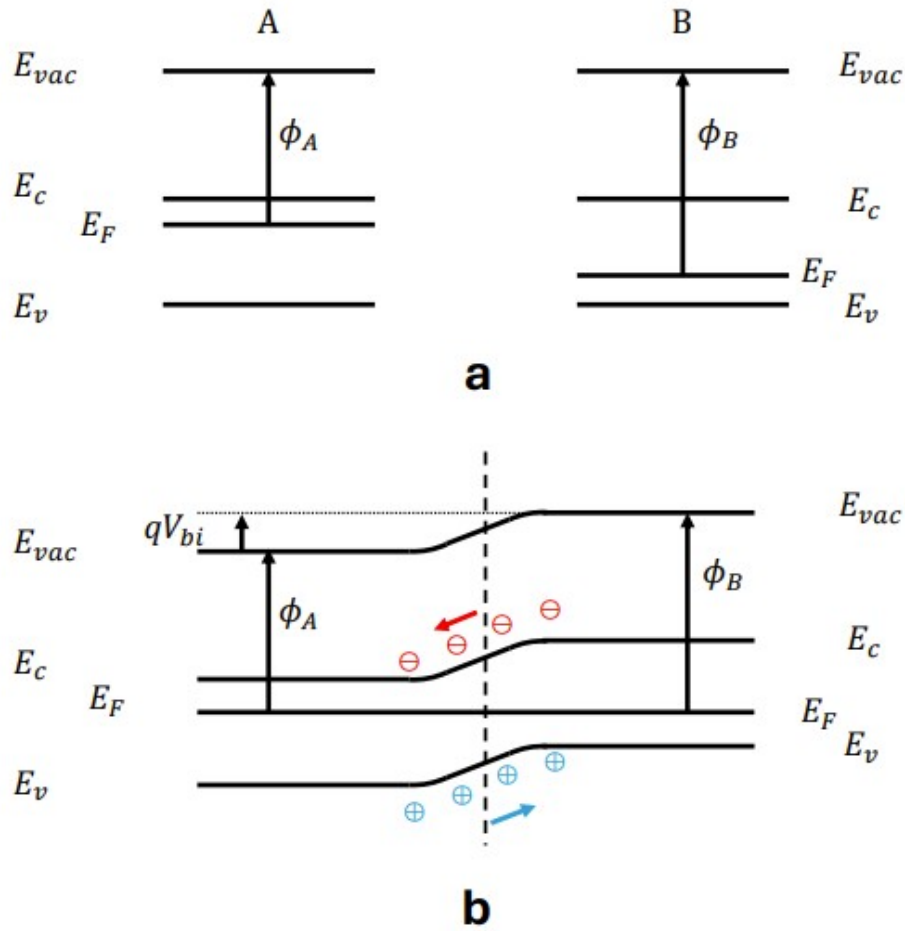


Figure 2.6: (a) Band profiles of Block A (n-type) and Block B (p-type) semiconductors in isolation. (b) Band profile of the p-n junction in equilibrium.

2.1.7 Charge Collection and Diode Behaviour

The p-n junction also functions as a diode, enabling charge extraction to the external circuit.

The ideal diode current density under dark conditions is

$$J_{\text{dark}} \approx J_0 \left(e^{qV/k_B T} - 1 \right), \quad (2.22)$$

where J_0 is the reverse saturation current density and V is the applied voltage. Under forward bias, the external field reduces the built-in field, allowing diffusion current to dominate and yielding a large net current. Under reverse bias, the current is limited to a small leakage current dominated by minority carriers.

$$J_{\text{dark}} \approx -J_0. \quad (2.23)$$

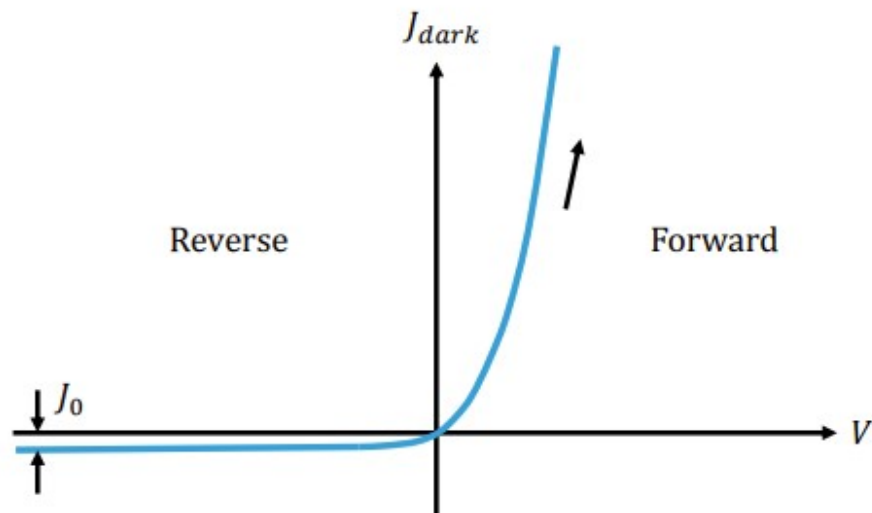


Figure 2.7: Plot of current density-voltage characteristic under dark conditions in the ideal p-n junction diode.

2.1.8 Solar Cell Operation (J, V, QE)

We can now consider the electrical behaviour of a solar cell under illumination. For a given bandgap, the maximum photocurrent density, J_{sc} , is determined by the number of photons absorbed and converted into charge carriers. This can be expressed as the integral of the external quantum efficiency (EQE), weighted by the incident photon flux and the elementary charge q :

$$J_{sc} = q \int_0^\infty \text{EQE}(\lambda) \frac{I(\lambda) \lambda}{hc} d\lambda \quad (2.24)$$

In the absence of illumination, a solar cell behaves as a diode under an applied bias. The resulting current increases exponentially with applied voltage and is described by the ideal diode equation:

$$J = J_{sc} - J_0 \left(e^{qV/(k_B T)} - 1 \right) \quad (2.25)$$

When the device is illuminated but operated under open-circuit conditions, the net current is zero. In this case, the photocurrent is exactly balanced by the diode (dark) current, and the maximum potential difference across the device is defined as the open-circuit voltage, V_{oc} . From the diode equation, this can be written as:

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{J_{sc}}{J_0} + 1 \right). \quad (2.26)$$

In practice, real devices deviate from this ideal behaviour due to various loss mechanisms. Series resistance reduces efficiency by limiting charge transport, which may arise from recombination within the bulk or poor charge extraction at interfaces. In addition, the assumption of infinite shunt resistance is not valid for real devices. Finite shunt resistance, often caused by leakage pathways such as pinholes, introduces additional current losses. These effects are captured in the modified diode equation:

$$J = J_{sc} - J_0 \left(e^{q(V + JAR_s)/(k_B T)} - 1 \right) - \frac{V + JAR_s}{R_{sh}} \quad (2.27)$$

The overall performance of a solar cell is determined by its ability to maximise power output. This is achieved by minimising series resistance and maximising shunt resistance. The device operates most efficiently at the maximum power point (MPP), which corresponds to the voltage and current at which the product JV is maximised. The ratio of this maximum power to the

product of V_{oc} and J_{sc} defines the fill factor (FF), which provides a measure of how closely the device approaches ideal behaviour.

The power conversion efficiency is therefore given by:

$$\eta_{\max}(E_g) = \frac{V_{oc}(E_g) \cdot J_{sc}(E_g) \cdot FF(E_g)}{\rho_{AM1.5}}, \quad (2.28)$$

where $\rho_{AM1.5}$ is the incident power density obtained by integrating the AM1.5 irradiance spectrum (Figure 2.8) over all wavelengths.

2.1.9 AM1.5 Spectrum

The above description can be applied to any light source. However, for photovoltaic applications we specifically want to consider the Sun as a light source once the light reaches the Earth's surface. As solar radiation travels from the Sun to the Earth, it is both attenuated and spectrally modified. The resulting spectrum, as a function of wavelength, is shown in Figure 2.8.

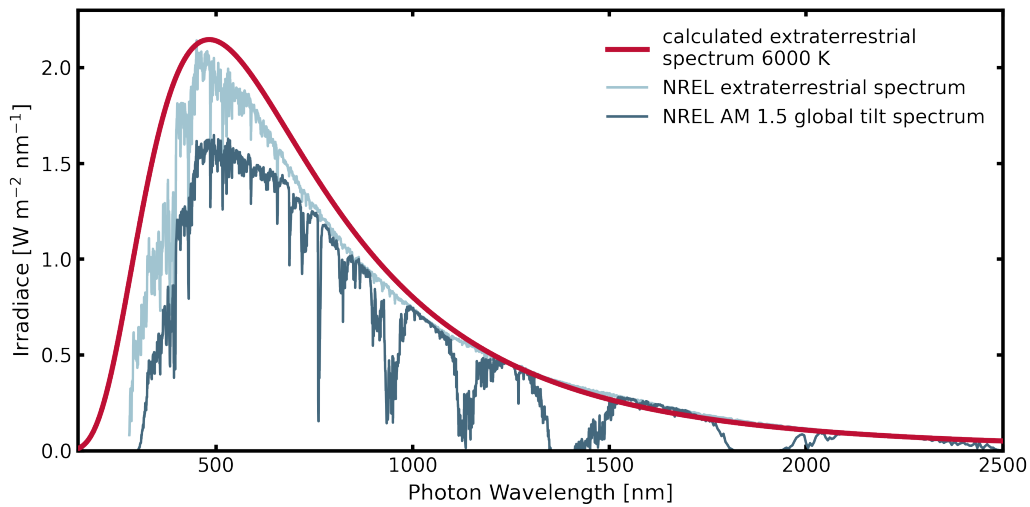


Figure 2.8: The AM1.5 solar spectrum based on the ASTM G173 standard, commonly distributed via NREL datasets. The NREL reference spectra for one sun outside the atmosphere (sun spectrum) and after travelling through 1.5 air mass (AM1.5 spectrum) are shown together with the wavelength spectrum calculated for a black body at $T = 6000$ K.²¹

Figure 2.8 compares the ideal blackbody spectrum with the measured solar spectrum. The discrepancies between the two arise primarily from absorption processes within the Sun and the atmosphere of the Earth. The sharp dips in intensity, known as Fraunhofer lines, correspond to absorption by atomic species in the outer layers of the Sun, such as sodium.²²

Upon entering the atmosphere, solar radiation undergoes additional scattering and absorption due to interactions with molecules and aerosols. These processes reduce the photon flux reaching the surface. Notably, the majority of solar power is concentrated in the visible range (400-700 nm), making materials that absorb efficiently in this region particularly suitable for photovoltaic applications.

2.1.10 Detailed Balance Limit

The interplay between the solar spectrum and semiconductor bandgap leads to a fundamental limit on solar cell efficiency. The quantum efficiency of a material describes the fraction of incident photons that generate charge carriers. However, only photons with energies greater than the bandgap (E_g) can be absorbed, corresponding to wavelengths shorter than a threshold value. Furthermore, excess photon energy above E_g is lost through thermalisation, as carriers relax to the band edges. This introduces an intrinsic trade-off: smaller bandgaps increase absorption but reduce output voltage, while larger bandgaps increase voltage but reduce absorption.

The combination of these effects defines the detailed balance limit, which describes the maximum achievable efficiency of a solar cell as a function of bandgap under standard illumination conditions. As an example, for a silicon cell with a bandgap of 1.1 eV the detailed balance limit is approximately 33%.¹²

2.1.11 Tandem Solar Cells

Tandem solar cells utilise multiple absorber layers with different band gaps to more efficiently convert the solar spectrum into electrical energy. Each sub-cell is designed to absorb photons with energies $E \gtrsim E_g$ close to its band gap, thereby minimising thermalisation losses associated with excess photon energy and transmission losses from sub-bandgap photons. By spectrally splitting the incident radiation across junctions, tandem architectures increase the maximum achievable efficiency beyond the single-junction Shockley–Queisser limit. In the limit of an infinite number of junctions, the detailed balance efficiency approaches $\sim 68\%$ ¹³; however, practical devices are typically limited to 2–4 junctions due to material, optical, and fabrication constraints.²³

For a two-junction tandem, two principal device architectures are employed: monolithic two-terminal (2T) and mechanically stacked four-terminal (4T) configurations. In both configurations the top cell has a larger bandgap than the bottom cell. In a 2T tandem, the sub-cells are connected in series via a recombination (tunnel) junction, enforcing current continuity such that the total current is limited by the sub-cell generating the lower photocurrent. This imposes a strict current-matching condition, requiring careful optimisation of the absorber band gaps, thicknesses, and optical management to balance photogenerated carrier densities. Additionally, the voltages of the sub-cells add, so the total open-circuit voltage is approximately the sum of the individual junction voltages.¹³

In contrast, a 4T tandem consists of electrically independent sub-cells, each with its own contacts, allowing independent operation at their respective maximum power points. This removes the current-matching constraint and enables more flexible material and design choices. However, 4T architectures introduce increased optical losses (e.g. from additional interfaces), greater fabrication complexity, and more demanding module integration.²⁴

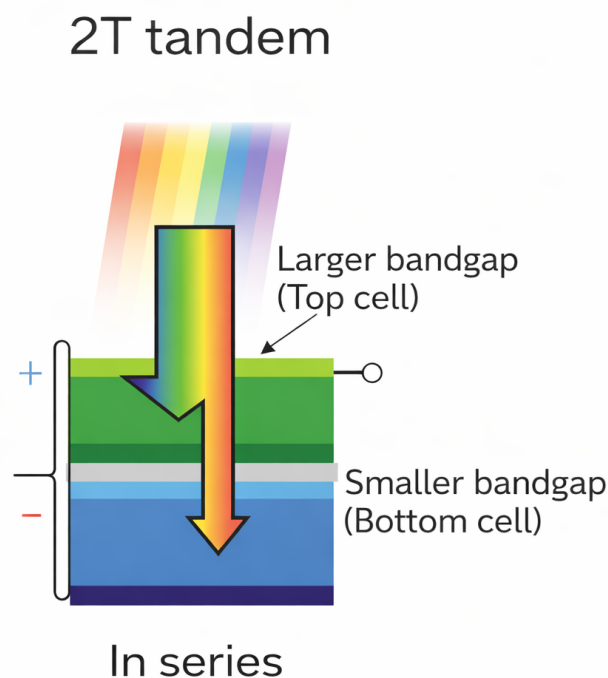


Figure 2.9: Schematic of a 2T tandem without a larger bandgap top cell and a narrower bandgap bottom cell.

2.2 METAL HALIDE PEROVSKITES

This section outlines the fundamental physics relevant to metal halide perovskites. It first describes the general perovskite crystal structure, before discussing the distinctive crystal and electronic structure of metal halide perovskites, which underpins their unique optoelectronic properties.

2.2.1 Structure

Perovskites are iono-covalent crystals described by the formula ABX_3 . Perovskites occur naturally, and the first discovered perovskite was $CaTiO_3$ in 1839. Since then, many other compositions have been discovered and synthesised.¹⁶ The Goldschmidt tolerance factor provides an approximate geometric criterion for the formation of perovskites at room temperature.

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)} \quad (2.29)$$

where r_i is the ionic radius of the ion at site A, B, or X. It was found empirically that perovskite structures form for $0.8 \leq t \leq 1$. At $t = 1$, the ideal cubic structure is formed. For $t > 1$, hexagonal face-sharing structures form, and for $t < 0.8$, ilmenite structures form, such as $FeTiO_3$.²⁵

Whilst the Goldschmidt tolerance factor indicates whether the A-site cation can fit into the perovskite structure, the octahedral factor informs us about the structural stability of the metal-halide octahedra. It is expressed as:

$$\mu = \frac{r_B}{r_X} \quad (2.30)$$

where r_B and r_X are the ionic radii of the B-site cation and X-site anion, respectively. Octahedra can form if $\mu > 0.41$.²⁶

In metal halide perovskites (MHPs), A is a monovalent cation, B is a divalent cation, and X is a monovalent anion. It is useful to outline the typical choices for MHPs:

A site: typically organic cations such as methylammonium (CH_3NH_3^+ , MA) and formamidinium ($\text{HC}(\text{NH}_2)_2^+$, FA), or inorganic cations such as Cs^+ .

B site: metal ions, typically Pb^{2+} or Sn^{2+} .

X site: halide ions, typically I^- , Br^- , or Cl^- .²⁶

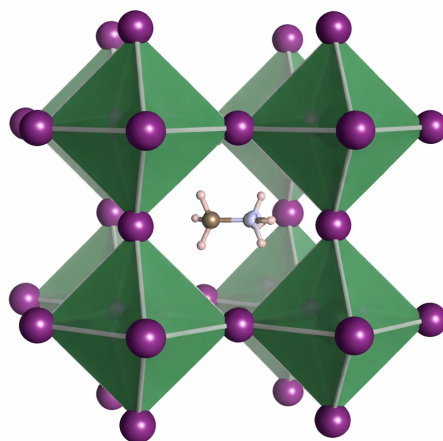


Figure 2.10: Schematic of the cubic crystal structure of MAPbI_3 . The purple spheres indicate iodide (halide), the centre of the green octahedra corresponds to lead (metal), and the octahedral void contains a methylammonium cation. This figure is reproduced with permission from Ref.²⁷

2.2.2 Optoelectronic properties

The suitability of metal halide perovskites (MHPs) for photovoltaic applications arises directly from their crystal and electronic structure. They are direct bandgap semiconductors with small exciton binding energies, typically on the order of a few millielectron volts at room temperature for compositions such as MAPbI_3 .²⁸ This behaviour originates from the high dielectric constant of the lattice, which screens the Coulomb interaction between electrons and holes, enabling rapid dissociation of excitons into free charge carriers.²⁹

The electronic band structure is governed by the interaction between metal and halide orbitals within the corner-sharing BX_6 octahedral framework. In APbI_3 systems, the conduction band minimum is primarily derived from Pb 6p orbitals, while the valence band maximum arises from antibonding interactions between Pb 6s and I 5p orbitals. More generally, changes in the composition of the BX_6 octahedra shift the positions of the valence and conduction bands. The diagram reproduced from Tao *et al.* illustrates how these band positions vary across different MHP compositions.³⁰ This antibonding character leads to highly dispersive bands, resulting in low effective

charge-carrier masses and, consequently, high carrier mobilities.³⁰

This same antibonding nature also underpins the defect tolerance of MHPs. Structural defects tend to introduce shallow states near the band edges rather than deep states within the bandgap, meaning they have a reduced impact on charge-carrier recombination. As a result, non-radiative losses are suppressed, enabling long carrier lifetimes and diffusion lengths.^{29,31}

The A-site cation, while important for structural stability and lattice dynamics, contributes little to the electronic states near the band edges. Instead, it influences the material indirectly through lattice distortions, dielectric screening, and dynamic disorder, all of which can affect charge-carrier behaviour.³⁰

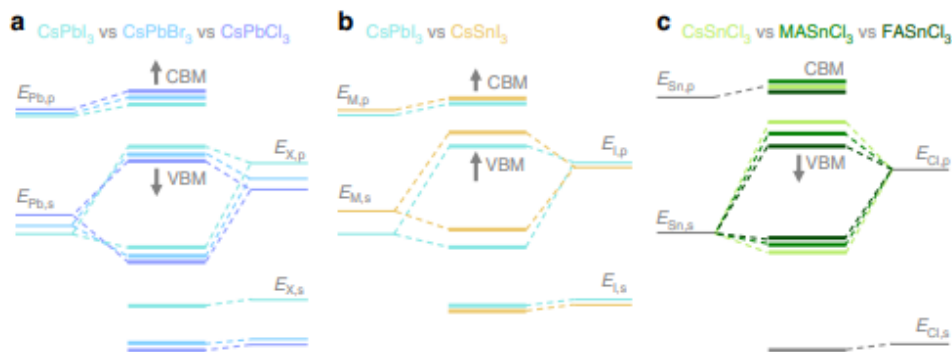


Figure 2.11: Schematic energy levels in MHPs. a, b represent trends in changing the halide anions and the metal cations, respectively, as identified from tight-binding analysis. c is an intuitive illustration of energy-level changes based on structural distortions in tin-based perovskites. Arrows indicate the shift in energy levels upon atom or small molecule substitution. This figure is reproduced from Tao *et al.*³⁰

2.2.3 Low-dimensional perovskites

Whilst the typical perovskite structure is the three-dimensional (3D) structure described above, lower-dimensional variants also exist. These include quasi-perovskite or layered perovskite structures, such as Ruddlesden–Popper and Dion–Jacobson phases. These materials exhibit interesting optoelectronic properties, as they allow tuning of the quantum well width and carrier confinement within the perovskite.³² Two-dimensional (2D) perovskites contain two distinct A-site cations (A' and A). They are formed when one of the cations is too large to fit into the cuboctahedral cavity of the conventional perovskite structure. As a result, the BX_6^{4-} octahedra can no longer maintain their corner-sharing connectivity. Instead, the large spacer cation induces the formation of a layered, quantum-well structure by separating slabs of BX_6^{4-} octahedra.³³ The thickness of

these slabs is described by the parameter n , which can range from 1 to ∞ , where the infinite case corresponds to the conventional 3D perovskite.

Although several types of 2D perovskites exist, distinguished by their crystal structures, the work in this thesis focuses on Ruddlesden–Popper (RP) phases. The general formula for an RP perovskite is $A'_2A_{n-1}B_nX_{3n+1}$, where A' is a large organic spacer cation, typically containing long alkyl chains or aromatic groups, and A , B , and X correspond to the conventional perovskite lattice sites.

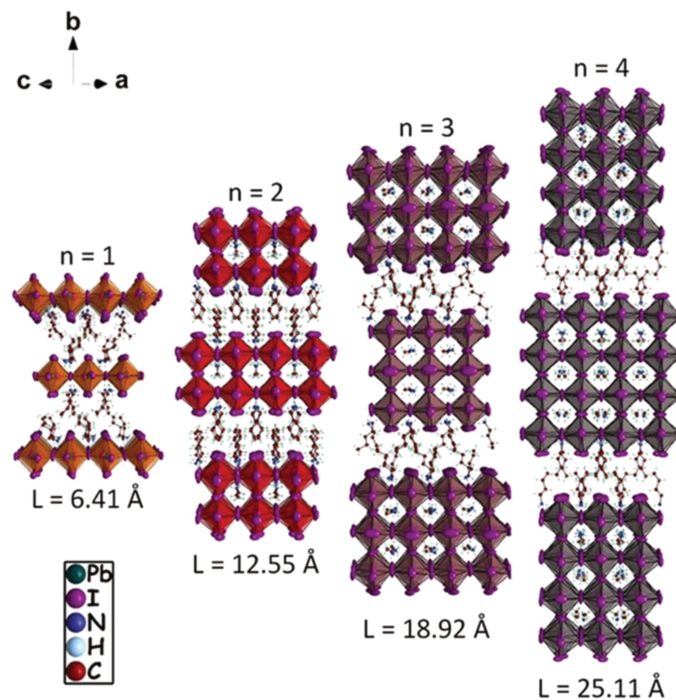


Figure 2.12: The crystal structure of $BA_2MA_{n-1}Pb_nI_{3n+1}$ Ruddlesden–Popper perovskites for $n = 1$ to $n = 4$. The figure is adapted from Stoumpos *et al.*³².

Owing to the insulating nature of the spacer cations, charge transport in 2D perovskites is highly anisotropic. Within the plane of the octahedral layers, the electronic properties are similar to those of their 3D counterparts. However, transport perpendicular to the layers is significantly hindered, leading to higher exciton binding energies and reduced charge-carrier mobility.³³

2.2.4 Lower symmetry phases

Perovskites can adopt phases other than those composed of corner-sharing octahedra. These are often referred to as polytypes and are typically undesirable or non-photoactive. They may form during crystallisation or arise as by-products of film degradation. A well-known example is the degradation of α -FAPbI₃ in ambient conditions into the non-photoactive δ -FAPbI₃ phase (2H

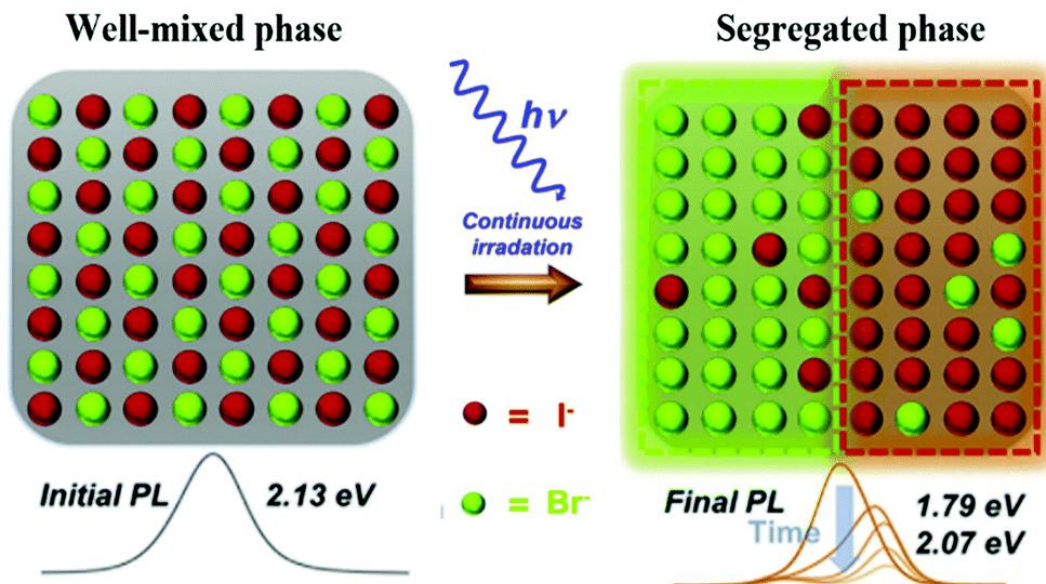


Figure 2.14: Schematic to show halide segregation under illumination in mixed iodide-bromide films. Figure reproduced from Uddin et al.³⁷

These defects provide pathways for halide migration, enabling segregation in mixed-halide compositions. The iodide-rich domains, which possess the smaller bandgap, can then quench the bromide-rich regions, adversely affecting device performance.³⁸ In FACs-based perovskites, this process typically occurs on longer timescales, owing to stronger bonding between the cations and the lead-halide octahedra, which increases the activation energy for ion migration and halide segregation.³⁹ When illumination is removed, halide-segregated systems can often relax back to a mixed-halide state.⁴⁰

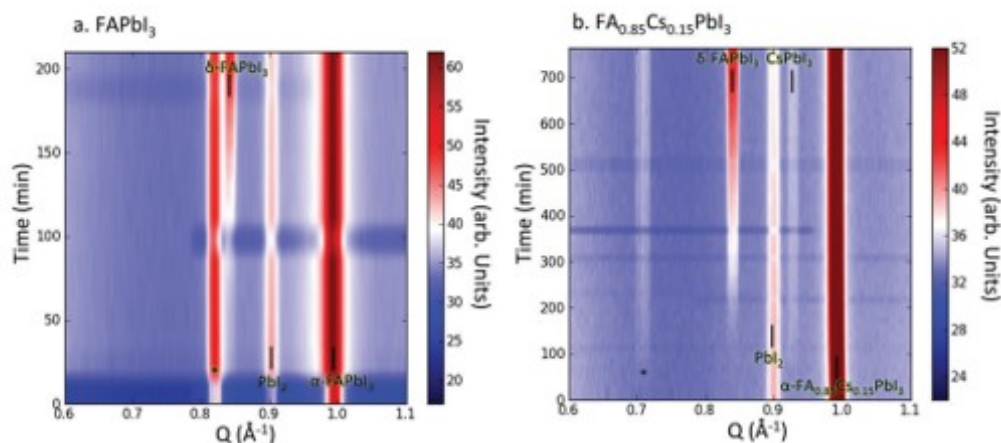


Figure 2.15: In situ X-ray diffraction of mixed A-site perovskite solar cells. X-ray diffraction profiles versus time of a. FAPbI₃ and b. FA_{0.85}Cs_{0.15}PbI₃. Figure reproduced from Liu et al.⁴¹

A-site segregation can also occur in FACs perovskites, leading to the formation of FA-rich and Cs-rich domains. It has been suggested that the nanoscale homogeneity of the initial film strongly influences its resistance to demixing, with better-mixed films generally showing greater resistance.⁴² In contrast to halide segregation, A-site segregation is typically irreversible, as FA-rich and Cs-rich domains can transform into thermodynamically stable non-perovskite phases at room temperature.³⁹

2.2.6 Impact of crystallisation dynamics on perovskite properties

The crystallisation dynamics of a perovskite play a critical role in determining the quality and properties of the resulting film.⁴³ Processing conditions directly influence crystallinity, defect density, and stability, and are therefore central to achieving high-performance devices.^{43,44} In general, two key considerations govern perovskite crystallisation. Firstly, films should exhibit good morphology, characterised by features such as low pinhole density. Secondly, the perovskite should have a low defect density. These factors are essential for achieving efficient charge transport and improved device stability.³¹

Crystallisation pathways can be modulated through a variety of approaches, most commonly through the use of additives, solvent engineering, and variation of the deposition method (e.g. vapour deposition or two-step solution processing).⁴⁵ These approaches influence nucleation and growth processes, often through the formation of intermediate phases that control film formation.⁴⁶

A simple example of a Lewis base-modulated process is the deposition of MAPbI₃ using dimethylformamide (DMF) with the addition of dimethyl sulfoxide (DMSO). As a stronger Lewis base, DMSO binds more strongly to PbI₂ than DMF, leading to the formation of Pb–DMSO complexes in the precursor solution.⁴⁷ This interaction slows the crystallisation process by increasing precursor solubility and stabilising intermediate phases, resulting in denser and more uniform films. In the absence of DMSO, nucleation proceeds too rapidly, preventing grain impingement and leading to rough, non-conformal polycrystalline films.⁴⁸

EXPERIMENTAL METHODS

3.1 FABRICATION

Materials and Chemicals

Lead iodide (PbI_2 , 99.9%, metal basis) and lead bromide (PbBr_2 , 99.9%, metal basis) were purchased from TCI Chemicals. Butylammonium iodide (BAI), butylammonium bromide (BABr), formamidinium iodide (FAI), formamidinium bromide (FABr), methylammonium iodide (MAI), and methylammonium bromide (MABr) were purchased from Greatcell Solar. Fullerene- C_{60} (C_{60} , 99.5%) and poly(methyl methacrylate) (PMMA) were purchased from Sigma-Aldrich. Caesium iodide (CsI, Sigma-Aldrich, 99.999%) and bathocuproine (BCP, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 98%) were purchased from Ossila. (4-(3,6-Dimethyl-9H-carbazol-9-yl)butyl)phosphonic acid (Me-4PACz) was purchased from TCI. All materials were used as received without further purification.

Perovskite and Film Fabrication

Substrate Cleaning Fluorine-doped tin oxide (FTO)-coated glass (Biotain, $30 \times 30 \times 1.1$ mm, $10\text{--}15 \Omega \text{sq}^{-1}$) was used as the substrate. The substrates were cleaned by sequential ultrasonication: 15 minutes in a 1% v/v Decon90 solution (in deionised water), followed by 15 minutes each in deionised water, acetone, and isopropyl alcohol. After cleaning, the substrates were dried with nitrogen gas and subsequently treated with UV-ozone for 30 minutes.

Preparation of Perovskite Films One-step $\text{FAPb}(\text{I}_x\text{Br}_{1-x})_3$

$\text{FAPb}(\text{I}_x\text{Br}_{1-x})_3$ films were prepared by dissolving PbI_2 , PbBr_2 , and FAI in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (4:1 DMF:DMSO). The precursor salts were weighed to yield a stoichiometric 1.3 M solution. Films were fabricated by dispensing $175 \mu\text{L}$ of precursor onto a spinning substrate after 5 s of a 1000 rpm (500 rpm s^{-1}) programme, followed by antisolvent quenching with $335 \mu\text{L}$ of anisole after 25 s of a second spin stage at 5000 rpm (1000 rpm s^{-1}) in a nitrogen-filled glovebox.

Two-step $\text{FAPb}(\text{I}_x\text{Br}_{1-x})_3$ PbI_2 and PbBr_2 were dissolved in DMF to yield a 1.2 M solution of the desired composition. Inorganic templates were fabricated by dispensing 175 μL of precursor onto a spinning substrate after 5 s of a 3000 rpm (500 rpm s^{-1}) programme, followed by annealing at 70 °C for 10 minutes. Subsequently, 300 μL of a 0.3 M FAI/FABr solution (at the desired halide ratio) was deposited onto the templates using spin coating (4000 rpm, 1000 rpm s^{-1} acceleration). The films were annealed at 150 °C for 15 minutes.

MeTHF-Templated Films 2-Methyltetrahydrofuran (1500 μL) was added to PbI_2 , MAI, and MABr, followed by *n*-butylamine (1.899 mmol, 187.6 μL), and the mixture was agitated until all solids were fully dissolved. A total of 50 μL of this solution was dynamically spin-coated onto glass substrates at 2500 rpm for 45 s in an environment with 20–22% relative humidity and temperature < 22 °C. The substrates were immediately annealed at 70 °C for 10 minutes. After cooling, the substrates were coated with 350 μL of a 0.1 M FAI/FABr solution in *n*-butanol (5000 μL total solvent). After 45 s of static soaking, the substrates were spun at 4000 rpm (1000 rpm s^{-1}) for 45 s, followed by annealing at 70 °C for 10 minutes and then 180 °C for 30 minutes.

MA-Based Ruddlesden–Popper Films ($\text{BA}_2\text{MAPb}_2(\text{I}_x\text{Br}_{1-x})_7$) Precursor solutions were prepared by dissolving BAI, BABr, PbI_2 , PbBr_2 , MAI, and MABr in DMF and N-methyl-2-pyrrolidone (NMP) (9:1 DMF:NMP) to yield a 0.6 M solution. Films were fabricated by dispensing 175 μL of precursor onto a spinning substrate after 5 s at 1000 rpm (500 rpm s^{-1}), followed by nitrogen gas quenching after 10 s of a second spin stage at 5000 rpm (1000 rpm s^{-1}) in a nitrogen-filled glovebox.

FA-Based Ruddlesden–Popper Films ($\text{BA}_2\text{FAPb}_2(\text{I}_x\text{Br}_{1-x})_7$) Precursor solutions were prepared by dissolving BAI, BABr, PbI_2 , PbBr_2 , FAI, and FABr in DMF and NMP (9:1 DMF:NMP) to yield a 0.6 M solution. Films were fabricated by dispensing 175 μL of precursor onto a spinning substrate after 5 s at 1000 rpm (500 rpm s^{-1}), followed by quenching with 800 μL of diethyl ether (DEE) after 10 s of a second spin stage at 5000 rpm (1000 rpm s^{-1}). Quenching requires a cut pipette tip and a slow dispensing rate ($\sim 1.5 \text{ s}$ for 800 μL) to achieve optimal film morphology. Films were annealed at 150 °C for 15 minutes.

FAPb(I_xBr_{1-x})₃ Precursor solutions were prepared by dissolving PbI₂, PbBr₂, FAI, and FABr in DMF and N-methyl-2-pyrrolidone (NMP) (9:1 DMF:NMP) to yield a 1.75 M solution. Films were fabricated using the same procedure as above, including DEE quenching and annealing at 150 °C for 15 minutes.

BA lead halide precursor Precursor solutions were prepared by dissolving 1 mole of: PbI₂, PbBr₂, BAI, and BABr in DMF and NMP (9:1 DMF:NMP) in the correct ratios (for each halide composition) to yield a 1.75 M solution.

2D/3D Templated Films FAPb(I_xBr_{1-x})₃ precursor was combined with BA lead halide precursor at the same halide fraction and molarity in a 1:1 ratio. Films were fabricated by dispensing 175 μL of precursor onto a spinning substrate after 5 s at 1000 rpm (500 rpm s⁻¹), followed by quenching with 800 μL of DEE after 15 s of a second spin stage at 5000 rpm (1000 rpm s⁻¹). Films were annealed at 100 °C for 10 minutes.

Converted Films (with Intermediate Anneal) Templated films were annealed at 180 °C for 15 minutes in a dry box (20% RH), then soaked for 45 s in a 0.1 M FAI_x:FABr_{1-x} solution in 1-butanol. Films were spun at 4000 rpm (1000 rpm s⁻¹) for 30 s, followed by annealing at 70 °C for 10 minutes and then 150 °C for 15 minutes.

Converted Films (without Intermediate Anneal) Templated films were soaked for 45 s in a 0.1 M FAI_x:FABr_{1-x} solution in 1-butanol, spun at 4000 rpm (1000 rpm s⁻¹) for 30 s, and annealed at 70 °C for 10 minutes followed by 180 °C for 15 minutes.

FA_{0.83}Cs_{0.17}Pb(I_{0.7}Br_{0.3})₃ Films were prepared by dissolving PbI₂, PbBr₂, FAI, and CsI in DMF:DMSO (4:1) to yield a 1.3 M solution. Films were fabricated using the same one-step protocol described above.

Sample Preparation for NMR Approximately 1 mg of perovskite material was dissolved in DMSO-*d*₆.

3.2 MATERIAL CHARACTERISATION

3.2.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a widely used analytical technique for determining the crystal structure, phase composition, and lattice spacing of materials. It relies on the interaction of X-rays with the periodic arrangement of atoms within a crystalline solid. In an XRD experiment, X-rays are produced within an X-ray tube and filtered to obtain radiation of a single wavelength. This beam is then collimated and directed onto the sample. As the X-rays penetrate the material, they are scattered by the electron density associated with the ordered atomic planes.¹⁸ Diffraction occurs when the scattered X-rays interfere constructively, generating detectable diffraction peaks. This condition is governed by Bragg's law:

$$n\lambda = 2d \sin \theta$$

where n is the diffraction order, λ is the wavelength of the incident radiation, d represents the spacing between crystallographic planes, and θ is the angle of incidence. By varying the angle θ and measuring the intensity of the diffracted X-rays, a diffraction pattern is obtained. These patterns are characteristic of the material's crystal structure and can be used for phase identification and structural analysis.

All XRD measurements presented in this thesis were performed using a PANalytical X'Pert powder diffractometer equipped with a Cu K α radiation source ($\lambda = 1.54 \text{ \AA}$), operating at 40 kV and 40 mA. The diffraction data were calibrated by aligning the 2θ axis with the primary FTO substrate peak at $2\theta = 26.6^\circ$.

3.2.2 UV–Vis Absorption

Ultraviolet–visible (UV–Vis) absorption spectroscopy is a widely used technique for probing electronic transitions in materials with a bandgap (E_g). In this work, measurements were performed

on thin films. When photons with energies equal to or greater than E_g are incident on the material, electrons are excited to the conduction band, resulting in optical absorption.

The absorbance (Abs) is calculated from the measured transmittance ($T = I/I_0$) using:

$$\text{Abs} = -\log_{10}(T)$$

It should be noted that, for thin films, this definition does not account for reflection losses and therefore represents an apparent absorbance rather than the intrinsic absorption of the material. Absorption spectra are typically plotted as absorbance versus wavelength (λ) or photon energy (E). Measurements in this work were carried out using a Bruker Vertex 80v FTIR spectrometer with a silicon diode detector, using a bare FTO-coated glass substrate as the reference.

3.2.3 Film Thickness Measurement by Stylus Profilometry

Film thicknesses were determined using a stylus profilometer (Dektak, Bruker). Prior to measurement, a step edge was created by mechanically removing a narrow strip of the perovskite film using a clean razor blade, exposing the underlying substrate. Care was taken to produce a well-defined edge while minimising additional damage to the surrounding film.

Samples were mounted on the profilometer stage, and line scans were performed perpendicular to the scratched region such that the stylus traversed from the bare substrate to the intact film surface. A low stylus force was employed to avoid deformation or scratching of the relatively soft perovskite layer. Scan lengths were chosen to ensure sufficiently flat baseline regions on both sides of the step.

The resulting height profiles were analysed using the instrument software. Film thickness was extracted as the vertical step height between the baseline corresponding to the exposed substrate and that of the film surface. Linear baseline corrections were applied where necessary to account for sample tilt. For each sample, measurements were taken at multiple locations across the substrate, and the reported thickness corresponds to the average value.

3.2.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to investigate the surface morphology of the perovskite layers and the cross-sections of the devices. In SEM, a focused beam of high-energy electrons is generated and rastered across the surface of the sample using electromagnetic lenses. As the incident electron beam interacts with the sample, various signals are produced through electron-matter interactions. In this work, imaging was performed in secondary electron (SE) detection mode using a Hitachi S-4300 microscope. Secondary electrons are low-energy electrons emitted from the near-surface region of the material, typically within a few nanometres of the surface. As a result, SE imaging is highly sensitive to surface topography and enables detailed visualisation of features such as grain size, surface roughness, and film coverage.

The intensity of emitted secondary electrons varies depending on the local geometry of the surface; regions with edges or protrusions emit more electrons and therefore appear brighter in the resulting image. By scanning the electron beam across the sample and collecting these signals, a high-resolution image of the surface morphology is obtained.

All measurements were performed under vacuum conditions to minimise scattering of the electron beam. This approach allows for nanoscale characterisation of both the perovskite films and device cross-sections, providing insight into structural features relevant to device performance.

3.2.5 Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton nuclear magnetic resonance (^1H NMR) spectroscopy was used to analyse the chemical composition of the perovskite samples. NMR is based on the interaction between nuclear spins and an external magnetic field. When placed in a strong magnetic field, hydrogen nuclei (protons) adopt discrete energy states depending on their spin orientation. Radiofrequency (RF) radiation is applied to the sample, and when the frequency matches the energy difference between these spin states, resonance occurs. Upon relaxation back to the lower-energy state, the nuclei emit a signal that is detected and converted into a frequency-domain spectrum via Fourier transformation.

The resonance frequency of each proton is influenced by its local electronic environment, resulting in a chemical shift that allows different chemical species to be distinguished. As such, ^1H NMR

provides information on molecular structure and composition. In this work, perovskite samples were dissolved in deuterated dimethyl sulfoxide (DMSO- d_6) prior to measurement. The use of a deuterated solvent minimises background signals from the solvent and provides a stable reference for the spectrometer. The resulting spectra were used to identify and quantify the organic cations present in the perovskite films.

3.2.6 Photoluminescence Quantum Yield (PLQY)

The photoluminescence quantum yield (PLQY) of a material is defined as the ratio of emitted photons to absorbed photons:

$$\text{PLQY} = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}}$$

PLQY measurements were carried out using a custom-built system incorporating an integrating sphere (Newport, 70682NS). Samples were positioned inside the sphere and excited from the perovskite side using a 532 nm continuous-wave laser (Roithner, RLTMILL-532, 2 W). The excitation intensity was corrected according to the bandgap of the sample to achieve a one-sun equivalent condition. The laser spot size was approximately 0.15 cm². The resulting photoluminescence emission was collected using a fibre bundle (Ocean Optics, QR600-7-SR125BX) and directed to a spectrometer (QE Pro, Ocean Optics). Measurements were performed at three different locations on each sample to ensure reproducibility and then averaged.

3.2.7 Steady-State and Time-Resolved Photoluminescence (SSPL and TRPL)

Steady-state and time-resolved photoluminescence (SSPL and TRPL) measurements were performed using a time-correlated single-photon counting (TCSPC) system (FluoTime 300, PicoQuant GmbH). SSPL measurements record the steady-state emission from a sample under continuous illumination, where photoexcited carriers relax to the band edges before recombining radiatively. This technique is sensitive to slower processes that influence emission intensity, such as trap states or ion migration.

TRPL measurements, in contrast, probe the time-dependent decay of photoluminescence following pulsed excitation, providing insight into charge-carrier recombination dynamics on nanosecond timescales. In these measurements, a pulsed laser excites the sample, and emitted photons are detected under single-photon counting conditions. The time delay between excitation and photon detection is recorded over many cycles to construct a decay profile.

All measurements were carried out using a 532 nm pulsed laser (LDH-P-C-532, PicoQuant GmbH) with repetition rates between 3 kHz and 1 MHz and a pulse width of < 100 ps. The excitation fluence was $4.93 \text{ nJ pulse}^{-1} \text{ cm}^{-2}$. Emission was collected at the peak wavelength using a monochromator coupled to a hybrid photomultiplier detector (PMA Hybrid 40, PicoQuant GmbH). The signal was attenuated to maintain a detector pile-up rate below 5%.

3.2.8 Photothermal Stress Aging of Films

PMMA-coated films were subjected to ageing under 85°C and 85% relative humidity using an environmental chamber equipped with a solar illumination source (ATLAS SUNTEST XLS+ aging box). The light intensity was maintained at one sun (100 mW cm^{-2}) throughout the ageing process.

3.3 DEVICE CHARACTERISATION

3.3.1 Device Current Density–Voltage Characteristics

Current–voltage (J – V) and maximum power point (MPP) measurements were performed using a Keithley 2400 source meter under ambient conditions, in both dark and illuminated environments. Illumination was provided by a Wavelabs SINUS-220 solar simulator, calibrated to 100 mW cm^{-2} using a certified KG3-filtered silicon reference photodiode (Fraunhofer ISE). The active device area was defined as 0.25 cm^2 using a black anodised metal aperture within a light-tight holder.

Measurements were conducted using an automated protocol. Dark J – V scans were carried out prior to illuminated measurements. The steady-state open-circuit voltage ($ss-V_{oc}$) was first determined by holding the device at zero current for 30 s. J – V sweeps were then performed in both reverse (forward bias to short circuit) and forward (short circuit to forward bias) directions over a voltage range of -1300 to 100 mV , with a scan rate of 300 mV s^{-1} . Following the J – V scans, maximum power point tracking was carried out for 30 s using a gradient descent algorithm. Finally, the short-circuit current density (J_{sc}) was recorded for 10 s at zero applied bias.

3.3.2 External Quantum Efficiency

The external quantum efficiency (EQE) of devices was measured using a Fourier-transform photocurrent spectrometer based on a Bruker Vertex 80v Fourier transform interferometer. The active area of devices (0.25 cm^2) was illuminated by a tungsten halogen lamp. The accurate EQE value was calibrated using a Newport calibrated reference silicon solar cell of known EQE.

The short-circuit current from the EQE measurement was determined by the overlap integral of the AM1.5 photon flux with the EQE. The bandgap was derived by taking the first derivative of the EQE with respect to wavelength and identifying the wavelength corresponding to the minimum value.

3.4 DATA ANALYSIS

3.4.1 Stretched Exponential Fitting for TRPL Analysis

The TRPL decay curves of various samples were modelled using a stretched exponential function:

$$I(t) = I_0 \exp \left[- \left(\frac{t}{\tau_c} \right)^\beta \right]$$

where $I(t)$ represents the photoluminescence intensity at time t , I_0 is the initial emission intensity, τ_c is a characteristic decay time, and β ($0 < \beta < 1$) describes the degree of dispersion in the recombination dynamics. Values of β less than unity indicate a broad distribution of decay processes, typically associated with energetic disorder or heterogeneous recombination pathways. An effective or average lifetime (τ_{avg}) was obtained from the fitted parameters using:

$$\tau_{\text{avg}} = \frac{\tau_c}{\beta} \Gamma \left(\frac{1}{\beta} \right)$$

where Γ is the gamma function, defined as:

$$\Gamma \left(\frac{1}{\beta} \right) = \int_0^\infty x^{\frac{1}{\beta}-1} e^{-x} dx$$

3.4.2 Elliott Fitting of Absorbance Data

The optical bandgap (E_g) of the perovskite films was determined by fitting the absorption edge using the Elliott model. In this approach, the absorption coefficient $\alpha(E)$ is described as the sum of contributions from bound excitonic states and continuum band-to-band transitions:

$$\alpha(E) = \alpha_X(E) + \alpha_C(E)$$

where $\alpha_X(E)$ represents discrete excitonic absorption below the band edge, and $\alpha_C(E)$ describes continuum absorption above the bandgap. In this work, the measured absorbance was used as a proxy for $\alpha(E)$ in the vicinity of the absorption onset.

Near the band edge, the continuum contribution dominates and follows the form:

$$\alpha(E) \propto \frac{1}{E} \cdot \frac{1}{1 - \exp\left(-2\pi\sqrt{\frac{E_b}{E-E_g}}\right)}$$

which incorporates Coulombic enhancement of absorption due to electron–hole interactions.

The total absorption was convolved with a broadening function to account for disorder and instrumental effects:

$$g(E) = \frac{1}{\cosh\left(\frac{E-E_g}{\gamma}\right)}$$

where γ is a phenomenological broadening parameter.

Fitting was performed over the spectral region surrounding the absorption onset, and the bandgap E_g was extracted as a fitting parameter corresponding to the onset of continuum absorption. In this analysis, the excitonic contribution was included to accurately reproduce the shape of the absorption edge, but only E_g was used for subsequent discussion.

3.4.3 Quantification of Organic Cations Using NMR

The relative composition of organic cations in the perovskite samples was determined using ^1H NMR spectroscopy. Spectra were obtained by dissolving the films in DMSO- d_6 , and characteristic proton resonances corresponding to each cation species were identified.

Quantification was performed by integrating non-overlapping peaks and normalising the integrals by the number of protons contributing to each signal. For butylammonium (BA), the terminal methyl ($-\text{CH}_3$) resonance was used, while formamidinium (FA) was quantified using its characteristic proton peak in the 8–9 ppm region. The relative molar ratios of the cations were then calculated from the normalised integrals. Care was taken to avoid peaks affected by overlap or proton exchange to ensure accurate quantification.

3.4.4 Peak Analysis Using Pseudo-Voigt Fitting

Diffraction peaks were analysed using OriginPro (OriginLab Corporation). Prior to fitting, a local background was subtracted using a linear baseline over a selected range encompassing each peak. Individual peaks were fitted using a pseudo-Voigt function, which models the peak shape

as a combination of Gaussian and Lorentzian components. Fitting was performed using a non-linear least-squares routine implemented within the OriginPro peak fitting module. The fitting parameters were allowed to vary freely within physically reasonable bounds to achieve optimal agreement with the experimental data. The peak position was obtained from the centre of the fitted function, while the integrated peak area was determined from the fitted peak profile. A consistent fitting procedure, including baseline selection and fitting range, was applied across all samples to ensure reliable comparison of extracted parameters.

3.5 COMPUTATIONAL MODELLING AND DATA GENERATION

3.5.1 α -Phase Dataset

For the α -phase, the existing training dataset of 3885 structures generated from ab initio molecular dynamics (AIMD) simulations was utilised.⁴⁹

3.5.2 δ -Phase Dataset

To generate training data for the δ -phase, on-the-fly AIMD simulations were performed using VASP’s built-in machine learning force field (MLFF) functionality. A two-stage approach consistent with the α -phase FAPb(I_{1-x}Br_x)₃ potential was employed: first, VASP’s Gaussian process regression-based MLFF was used for exploratory data generation, and then a production MACE model was trained on the collected dataset.⁵⁰

$1 \times 2 \times 2$ supercells of δ -FAPb(I_{1-x}Br_x)₃ were employed (containing the same number of formula units as the $2 \times 2 \times 2$ α -phase supercells used in the α -phase training) across three bromide concentrations: 0%, 50%, and 100% Br. During each 25 ps MD trajectory, most force evaluations were performed by VASP’s on-the-fly MLFF using the evolving machine-learned potential, while configurations with MLFF uncertainty above a threshold were automatically identified by Bayesian error estimation. For these uncertain configurations, full DFT calculations were performed and added to the MLFF training set in real time, allowing the potential to be improved continuously during the simulation. The structures selected for DFT evaluation via this Bayesian active learning procedure were extracted and used as the δ -phase training dataset. Efficient sampling of the

configurational space was therefore ensured, while DFT calculations were concentrated on the most informative structures. The final δ -phase training set comprised 2340 structures selected via Bayesian active learning.

3.5.3 MACE Model Training

The combined training dataset of 6225 structures (3885 α -phase + 2340 δ -phase) was split into training (68%), validation (16%), and test (16%) sets. The split was performed separately for each phase to ensure balanced representation of both structural polymorphs in all subsets.

A MACE model was trained using a radial cutoff of 6.0 Å, two message-passing layers with 64 channels per layer (hidden irreps: $64 \times 0e + 64 \times 1o$). The model was trained for up to 1000 epochs using the AMSGrad optimizer.⁵¹ For details of the training protocol, including all hyperparameters, see the MACE training line provided below.

The final model achieved root-mean-square errors (RMSE) of 0.1 meV/atom for energies and 5.8 meV/Å for forces on the combined phases test set.

3.6 MIXING ENTHALPY AND FREE ENERGY CALCULATIONS

3.6.1 Thermodynamic Framework

The thermodynamic quantities governing halide mixing are defined as follows. The mixing enthalpy is calculated from the dynamically averaged energies of the mixed system and the pure end members:

$$\Delta H_{\text{mix}} = H_{(x_a, x_b)} - x_a H_{(x_a=1)} - x_b H_{(x_b=1)}. \quad (3.1)$$

where $H_{(x_a, x_b)}$ denotes the enthalpy of the mixed system with halide fractions x_a (I^-) and x_b (Br^-), and $H_{(x_a=1)}$ and $H_{(x_b=1)}$ correspond to the pure iodide and bromide end members, respectively. The configurational entropy of mixing, assuming ideal random mixing on the halide sublattice, is given by:

$$\Delta S_{\text{mix}} = -k_{\text{B}} (x_a \ln x_a + x_b \ln x_b). \quad (3.2)$$

where k_B is the Boltzmann constant. The Gibbs free energy of mixing at temperature T is then:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}. \quad (3.3)$$

3.6.2 Static Configurational Sampling

To compute mixing enthalpies, extensive configurational sampling was performed at 25 equally spaced bromide concentrations ($x = 0.00, 0.042, 0.083, \dots, 0.958, 1.00$) corresponding to all possible integer substitutions in the supercells. The same supercell sizes as used in training were employed: $2 \times 2 \times 2$ for the α -phase and $1 \times 2 \times 2$ for the δ -phase, both containing 24 halide sites. At each concentration, 50 random I/Br distributions were generated and geometry optimisations were performed using the trained MLIP, giving 2500 optimisations in total. For each polymorph, the lowest-energy structure at each concentration was selected for subsequent molecular dynamics calculations.

3.6.3 Molecular Dynamics Simulations for Dynamic Mixing Energies

To incorporate dynamic contributions to the mixing energetics, including vibrational and rotational effects from octahedral tilting and FA cation reorientation, NPT molecular dynamics were performed on each statically selected structure.

All NPT simulations were conducted using ASE (Atomic Simulation Environment) with the Nosé-Hoover chain thermostat and barostat implementation (MTKNPT).^{52,53} Simulations were maintained at a temperature of 300 K and a pressure of 1 bar, with thermostat and barostat damping times of 50 fs and 500 fs, respectively. A timestep of 0.5 fs was used for all MD runs. Each composition was equilibrated for 200 ps, after which the total energies were averaged over the final 100 ps to obtain time-averaged internal energies for the computation of dynamic mixing enthalpies, ΔH_{mix} .

The thermodynamic mixing quantities were evaluated as a function of the bromide fraction x using the standard definitions for binary mixtures. Since ΔH_{mix} was calculated via dynamic NPT simulations, both static energetic effects and finite-temperature dynamic contributions arising from vibrations and molecular rotations were captured.

3.6.4 Simulations of 2D Perovskite Template $\text{BA}_2\text{FAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$

For the 2D template $\text{BA}_2\text{FAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$, a similar computational workflow was employed using a MLIP from Karimatarsi et al.⁵⁴ The supercell contained 28 halide sites, and 50 random halide distributions were generated at each concentration. NPT molecular dynamics were performed on the lowest-energy configuration at each composition using identical simulation parameters to those described above for $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$. This same potential was used to simulate thermal expansion of the 2D perovskite structure by an NPT simulation at $T = 500$ K.

THE MISCIBILITY GAP IN



4

4.1 INTRODUCTION

As mentioned in the Theory section, MHPs are direct bandgap semiconductors with excellent optoelectronic properties, such as high charge-carrier mobilities, long carrier lifetimes, low trap densities, and a tunable bandgap. The tunability of the bandgap enables their use in single- and multi-junction devices through compositional engineering of the ABX_3 structure.^{55–57} For instance, formamidinium lead trihalide (α -FAPbI₃) has a bandgap of 1.48 eV⁵⁸, which is close to optimal for a single-junction device. This has been demonstrated in recent work in which stable devices with efficiencies exceeding 25% have been reported, although these studies use small amounts of other cations such as MA and Cs.^{23,59} In multi-junction tandem cells, multiple semiconductors with different bandgaps are utilised to harness a greater portion of the solar spectrum. As a result, tandem architectures can exceed the theoretical efficiency limit of single-junction devices, enabling higher power output per unit area.⁶⁰ Referring to the Theory chapter, for two-terminal tandems, the top and bottom cells must satisfy the current-matching condition. This requires careful selection of the bandgaps to maximise the overall power output and avoid limitation by the sub-cell producing the lower photocurrent.

In principle, bandgap widening in perovskites can be achieved by partial substitution of bromide (Br^-) for iodide (I^-) at the X-site. Through this compositional variation, perovskites with bandgaps ranging from approximately 1.5 eV (FAPbI₃) to 2.2 eV (FAPbBr₃) can be fabricated.^{27,60} However, it has been shown that, unlike MA-based perovskites, the photoactive α -phase of FA-based perovskites cannot be crystallised across the entire compositional range from pure iodide to pure bromide.⁶¹ Instead, for compositions containing 20%–60% bromide, a pronounced deviation from Vegard’s law is observed, referred to as the ‘miscibility gap’.

The primary structural difference between the two cations is that FA (ionic radius 253 pm)⁶² is larger than MA (ionic radius 217 pm)⁶²; however, beyond this observation, no comprehensive explanation has been proposed to account for the origin of the miscibility gap. Attempts to explain the miscibility gap have not fully accounted for all experimental observations. For example, the Goldschmidt tolerance factor of FAPbI₃ is approximately 0.99 (although an exact value is

difficult to determine due to the non-spherical nature of the FA cation), placing it near the upper limit of structural stability for the perovskite phase. This has been proposed as a reason for the metastability of α -FAPbI₃ and the preference for the δ -phase at room temperature.¹⁵

However, this explanation cannot account for the miscibility gap, as incorporation of bromide reduces the tolerance factor; therefore, increasing bromide content should promote the crystallisation of the α -phase. In previous computational studies, it has been argued that the mixing enthalpy of the photoactive phase is sufficiently large to render certain iodide-bromide ratios unstable, thereby creating a miscibility gap in FAPb(I_{1-x}Br_x)₃.⁶³ However, these studies were performed at 0 K using density functional theory (DFT), and thermal effects arising from lattice vibrations and molecular reorientation were not included. Furthermore, when the same approach is applied to MA-based perovskites, a similar gap is predicted, despite these compositions mixing well experimentally.²⁷ This discrepancy highlights that the origin of the miscibility gap cannot be fully explained using existing models. More recently, finite-temperature contributions to the mixing enthalpy of α -FAPb(I_{1-x}Br_x)₃ have been incorporated using machine-learning interatomic potentials (MLIPs), which account for vibrational and rotational effects.⁴⁹ In that study, no miscibility gap was predicted at room temperature, suggesting that the origin of the miscibility gap may not lie in the intrinsic thermodynamic instability of the α -phase. Nevertheless, a complete physical explanation remains lacking.

Not only is the miscibility gap not well understood, but there are currently no general processing methods to circumvent it without using a mixed A-site cation. Therefore, in this chapter, alternative crystallisation pathways are explored in an effort to produce α -FAPb(I_{1-x}Br_x)₃ across the entire iodide-bromide compositional space. Such approaches have previously been utilised to overcome unfavourable kinetics and stabilise targeted polymorphs in materials such as manganese oxide (MnO₂).⁶⁴ A similar effect was recently demonstrated by Gallant *et al.* in the case of FAPbI₃.⁶⁵ By employing 2D perovskite thin films as crystallisation templates and subsequently converting them into 3D perovskites, kinetic stabilisation of the α -phase can be achieved, suppressing the transition to the δ -phase.^{65,66}

Compositions currently employed to achieve stable, high-efficiency devices within the miscibility gap region (1.6-2.0 eV) are based on mixed A-site and mixed-halide systems. A typical example is $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$.⁶⁷ Although impressive performance has been demonstrated for these mixed A-site compositions, concerns regarding their long-term operational stability remain. In studies conducted on $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$, A-site demixing has been observed in films and devices subjected to photothermal stress.^{39,42} The initially macroscopically homogeneous system was shown to segregate into two distinct non-photoactive hexagonal phases, δ -FAPbI₃ and δ -CsPbI₃, thereby degrading long-term performance.⁶⁸ Concurrently, it has been suggested that A-site demixing may catalyse halide segregation, which can further reduce device performance.³⁹

In this chapter, the miscibility gap is first experimentally verified and subsequently characterised. To elucidate its origins, MLIP models are employed to investigate the thermodynamics of halide mixing in both the photoactive (α) and non-photoactive (δ) phases of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$. This approach differs from previous models, in which only the α -phase was considered.⁴⁹ It is found that the miscibility gap corresponds to the compositional region in which the halide mixing enthalpy of the δ -phase becomes comparable to that of the α -phase. As a consequence, a degeneracy in the Gibbs free energy arises, leading to the formation of less crystalline films which contain both the α -phase and polytypes. To address this issue, various crystallisation pathways are explored to kinetically stabilise the α -phase. The processing conditions are iteratively refined through modification of the number of processing steps, adjustment of the solvent system, and the introduction of 2D templates and specific annealing protocols.

4.2 RESULTS AND DISCUSSION

4.2.1 Understanding the origins of the miscibility gap

To experimentally verify the existence of the miscibility gap, $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films were fabricated across the entire compositional range, from neat iodide ($x = 0$) to neat bromide ($x = 1$). The films were processed by spin-coating a precursor ink containing the desired precursor salts (combined in the appropriate molar ratios) dissolved in dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) (9:1 DMF:NMP), in conjunction with a diethyl ether (DEE) anti-solvent quench. Full fabrication details are provided in the Experimental Methods chapter. Images of the films are shown in Figure 4.1.

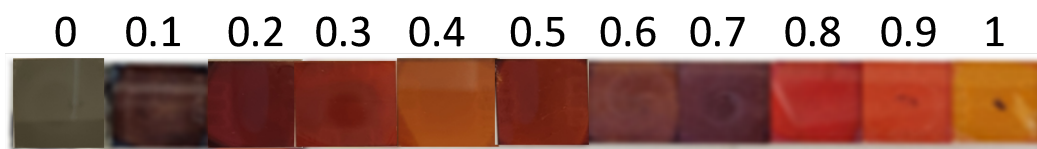


Figure 4.1: Photographs of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from DMF/NMP with increasing Br incorporation. From left to right, FAPbI_3 ($x = 0$) to FAPbBr_3 ($x = 1$) in increasing 10% Br increments.

The structural and optical properties of the films were investigated using X-ray diffraction (XRD) and ultraviolet–visible absorption spectroscopy (UV–Vis). The diffractograms for the full compositional range are shown in Figure 4.2.

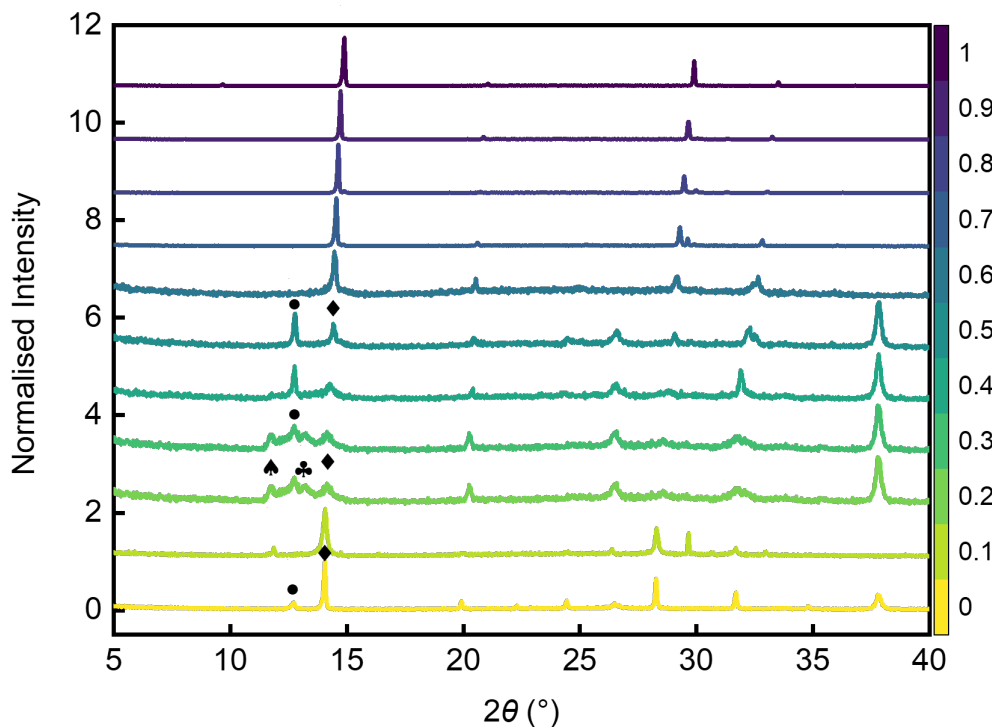


Figure 4.2: X-ray diffractograms of a series of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. Normalised XRD patterns prepared from DMF/NMP with increasing Br incorporation. From bottom (yellow) FAPbI_3 to top (purple) FAPbBr_3 in 10% increments. The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase, circle – (001) PbI_2 , spade – (100) 2H (δ -phase), club – (101) 4H. (For ease of visualisation, some phases are only marked in certain samples, even if they exist elsewhere.)

Figure 4.2 shows that different compositions contain varying numbers of phases. The region of interest is between 11° and 15° . Some compositions, such as the 0% Br sample (FAPbI_3), exhibit only reflections corresponding to the (100) cubic α -phase (at 14°) and the (001) PbI_2 peak (at 12.7°). The 10% Br composition still shows a strong α -phase reflection; however, a new peak appears at 11.8° , which is not present in the 0% sample. This corresponds to the (100) reflection of the 2H phase, also referred to as the δ -phase.³⁵

The 20% to 40% Br compositions exhibit the greatest number of reflections. In both cases, the α -phase reflection has significantly lower intensity. In addition to the three phases mentioned above, these compositions show an additional peak at 13.2° , corresponding to the (101) reflection of the 4H phase.³⁵ For the 40% Br composition, the α -phase reflection remains lower in intensity, the PbI_2 reflection increases in intensity, the 4H and the 2H reflections decrease in intensity.

For the 50% Br composition, only the α -phase and PbI_2 reflections are observed; however, the relative intensity of the PbI_2 reflection is higher than that of the α -phase. From 60% to 100% Br composition, the α -phase reflection is strong and no additional peaks are observed.

To quantify the presence of polytypes relative to the α -phase across compositions, the relative phase fractions were estimated by comparing the integrated peak areas obtained from pseudo-Voigt fitting of the α -phase and 2H polytype reflections. The resulting ratio was plotted as a function of composition in Figure 4.3. As the 2H phase (δ -phase) was observed across the widest compositional range, it was selected as the reference for comparison. Although this analysis provides only a qualitative estimate of the relative phase fractions, it offers a useful basis for comparing trends across the compositional series.

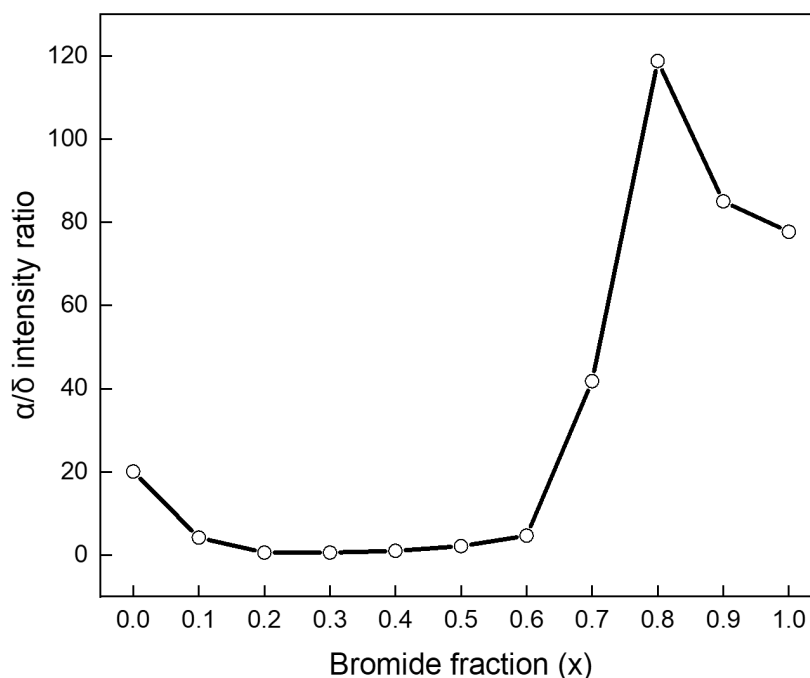


Figure 4.3: Relative intensity of (100) α - and (100) 2H phase reflections across a series of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. Relative intensity of α -phase and 2H phase plotted against bromide fraction (x) for $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films were made via 1-step processing from DMF/NMP. The peak position and integrated peak areas were calculated using a pseudo-Voigt fit.

Figure 4.3 shows that the α -phase is most suppressed relative to the δ -phase in the compositional range between 10% and 60% bromide. In contrast, for compositions containing more than 60% bromide, the α -phase becomes dominant. This suggests that, within this intermediate compositional range, the crystallinity of the α -phase is reduced, while that of the δ -phase is enhanced.

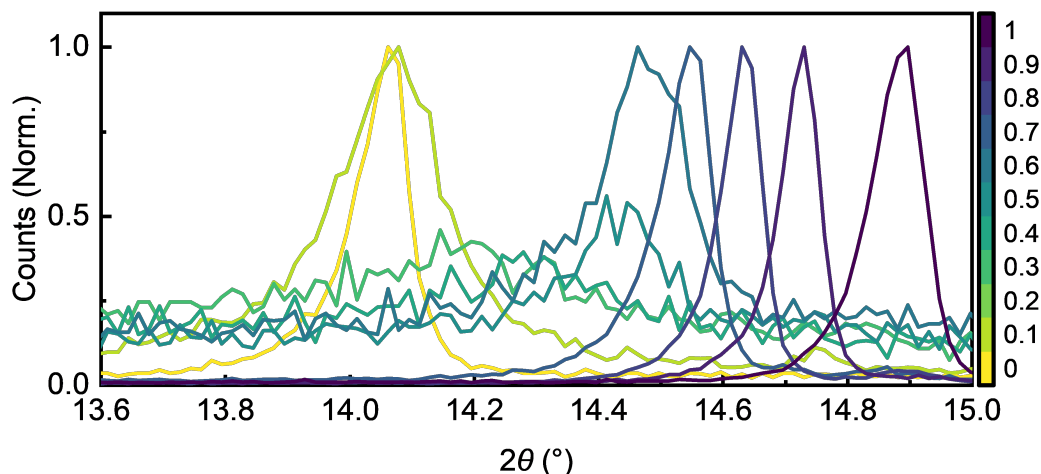


Figure 4.4: XRD patterns highlighting the α -phase reflection of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. Normalised XRD patterns between 13.6° and 15° of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from DMF/NMP via one-step processing with increasing Br incorporation. From left (yellow pattern of FAPbI_3) to right (purple pattern of FAPbBr_3) in increasing increments of 10% Br.

Focusing on the region where the (100) α -phase reflections are observed (between 13.6° and 15°) in Figure 4.4, a reduction in peak intensity accompanied by peak broadening is evident for compositions in the range $0.1 \leq x \leq 0.6$. This supports the observation of reduced α -phase crystallinity within this compositional range. Moreover, the peak intensity reaches a minimum for compositions near the centre of this range (30–40% Br).

The peak broadening is quantified in Figure 4.5, where the full width at half maximum (FWHM) of the α -phase reflection is plotted across all compositions. The trend shows that the peaks broaden from 0% to 20% bromide, are broadest between 20% and 40%, and then become progressively sharper from 40% to 70%. From 70% to 100%, the peaks are as sharp as those of the 0% sample. The combination of peak broadening and reduced α -phase intensity indicates increased structural disorder and reduced crystallinity.

These observations are consistent with previous reports in the literature. Suppression of the α -phase has been observed by McMeekin *et al.* and Eperon *et al.*^{60,61}; however, although multiple phases were present in their XRD patterns, these were not attributed to the presence of polytypes. In contrast, the results presented here demonstrate that, within the miscibility gap region, the suppression and broadening of the α -phase reflection are coupled to the presence of polytypes in the films. Furthermore, the extent of α -phase suppression correlates with both the number of polytypes present and the intensity of their reflections. In the films studied in this section, the

miscibility gap spans compositions between 10% and 60% bromide, with the greatest suppression of the α -phase occurring for compositions between 20% and 40% Br.

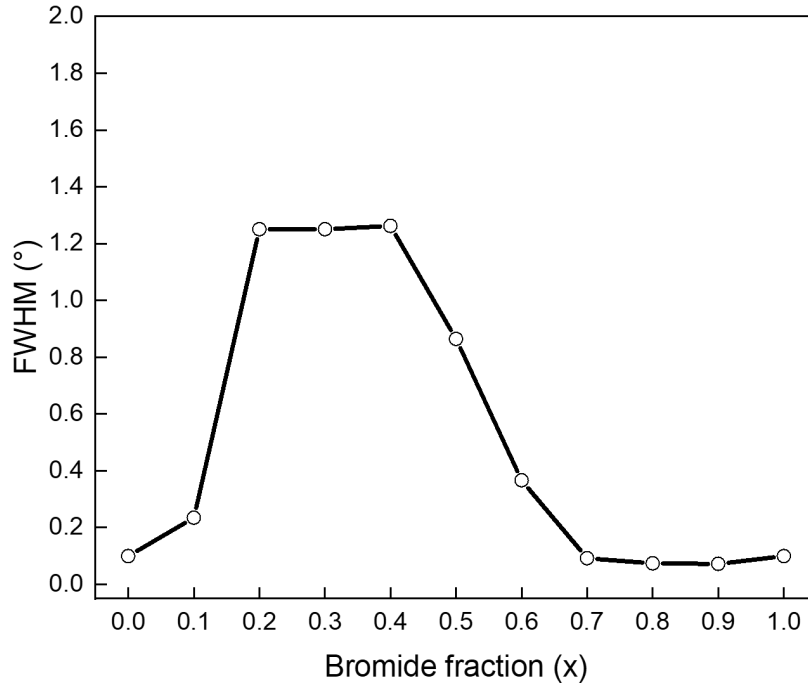


Figure 4.5: Full width at half maximum of the (100) α -phase reflections across a series of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. FWHM of α -phase reflections plotted against the bromide fraction of the composition for films prepared via one-step processing from DMF/NMP. The FWHM was calculated using a pseudo-Voigt fit.

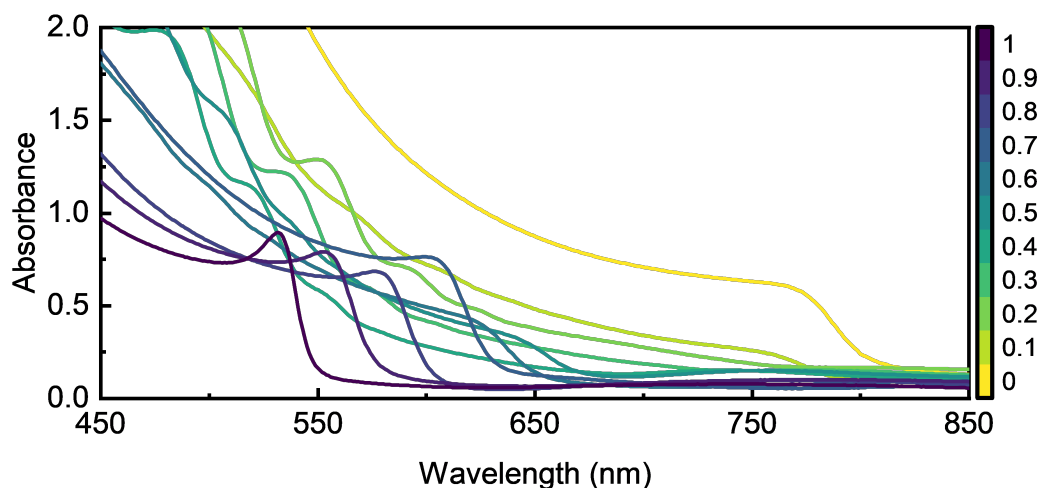


Figure 4.6: UV–Vis absorbance spectra of a series of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. The films were prepared from DMF/NMP with increasing Br incorporation. From right (yellow pattern of FAPbI_3) to left (purple pattern of FAPbBr_3) in increasing increments of 10% Br.

The suppression of the α -phase is also reflected in the UV–Vis absorbance data shown in Figure 4.6. A sharp absorption onset is observed for the 0% Br composition; however, this sharpness is partially reduced in the 10% Br sample. Between 20% and 40% Br, the absorption onset becomes significantly less well defined. The 50% and 60% Br compositions show a partial recovery, with absorption onsets similar to that of the 10% Br sample. The sharp onset is fully recovered for compositions between 70% and 100% Br.

The trends in the absorption spectra closely follow the suppression of the α -phase reflection observed in XRD measurements. In particular, the compositional range between 20% and 40% Br, where polytypes are most prevalent, corresponds to the weakest and least well-defined absorption onsets.

Taken together, the XRD and UV–Vis measurements indicate that the miscibility gap corresponds to a compositional region in which the α -phase exhibits reduced crystallinity. This builds upon previous observations of the miscibility gap, while demonstrating a clear link between the crystallinity of the α -phase and the presence of polytypes in the films.

Computational modelling of the miscibility gap

All computational calculations were conducted by Tobias Loeff (Department of Materials, University of Oxford). See Chapter 3 for full details.

To investigate the origin of the miscibility gap based on previous computational modelling, an ab initio-trained MLIP was used to probe the energetics of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ across the full halide mixing range, from pure iodide to pure bromide. Unlike earlier DFT-only treatments^{27,63}, these potentials allow a much larger portion of the configurational space associated with I/Br site disorder to be sampled. They also enable finite-temperature, molecular-dynamics-based evaluations of the mixing enthalpy (ΔH_{mix}), incorporating vibrational and rotational contributions. This approach is similar to the recent work mentioned above, in which MLIP was used to demonstrate that no thermodynamic instability exists in $\alpha\text{-FAPb}(\text{I}_{1-x}\text{Br}_x)_3$.⁴⁹ However, in the present study, the approach was extended to consider the thermodynamics of both the α - and δ -phases.

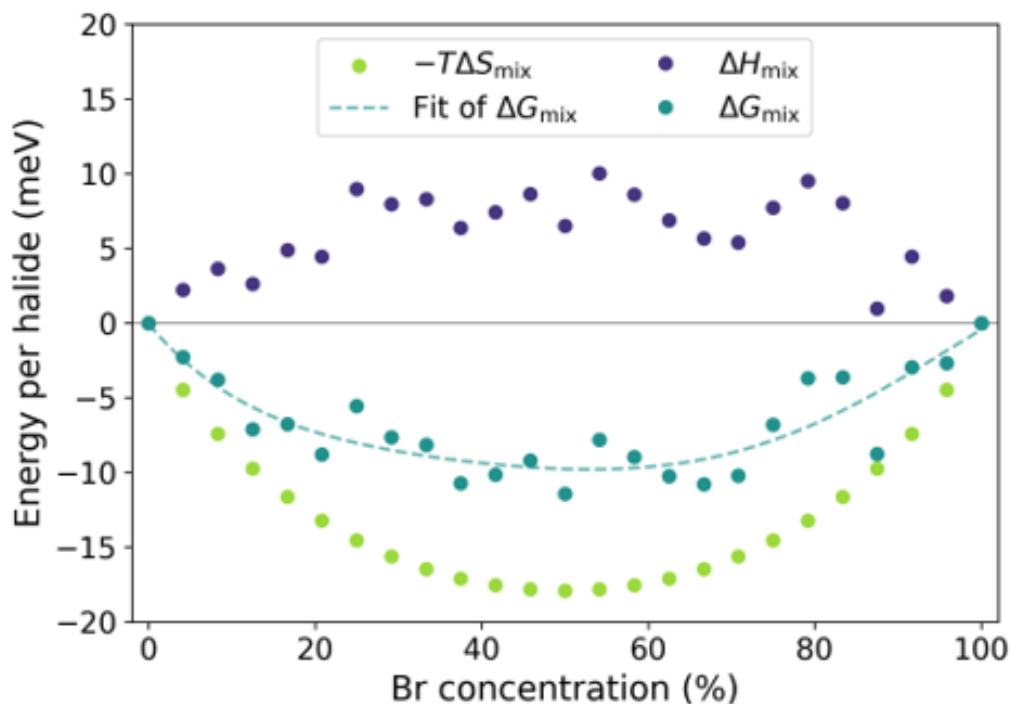


Figure 4.7: Computed Gibbs free energy of mixing for the α -phase. Thermodynamic contributions including enthalpy and entropy at 300 K across the full bromide composition range. Calculations were done by Tobias Loeff (Department of Materials, University of Oxford).

The calculated Gibbs free energy of mixing (ΔG_{mix}) at 300 K for the α -phase is shown in Figure 4.7. From the figure, it is apparent that the configurational entropy term ($-T\Delta S_{\text{mix}}$) outweighs the mildly positive mixing enthalpies at all Br concentrations, resulting in a negative Gibbs

free energy of mixing that becomes increasingly negative towards the midpoint composition. This indicates that, if only the thermodynamics of the α -phase are considered, as in the aforementioned modelling study, a miscibility gap should not exist at 300 K.⁴⁹

This prediction of full miscibility contradicts experimental observations, demonstrating that consideration of the α -phase alone is insufficient to explain the presence of the miscibility gap. However, the experimental data in the previous section suggest that, following crystallisation, films within the miscibility gap contain a mixture of the α -phase and various polytypes. This indicates that considering only the thermodynamics of the α -phase is insufficient to explain the miscibility gap. To address this, the same MLIP modelling approach is applied to the 2H polytype (δ -phase). This phase is selected because it is the most prevalent across the compositional range, in contrast to the 4H polytype, which is only observed in the central region of the gap.

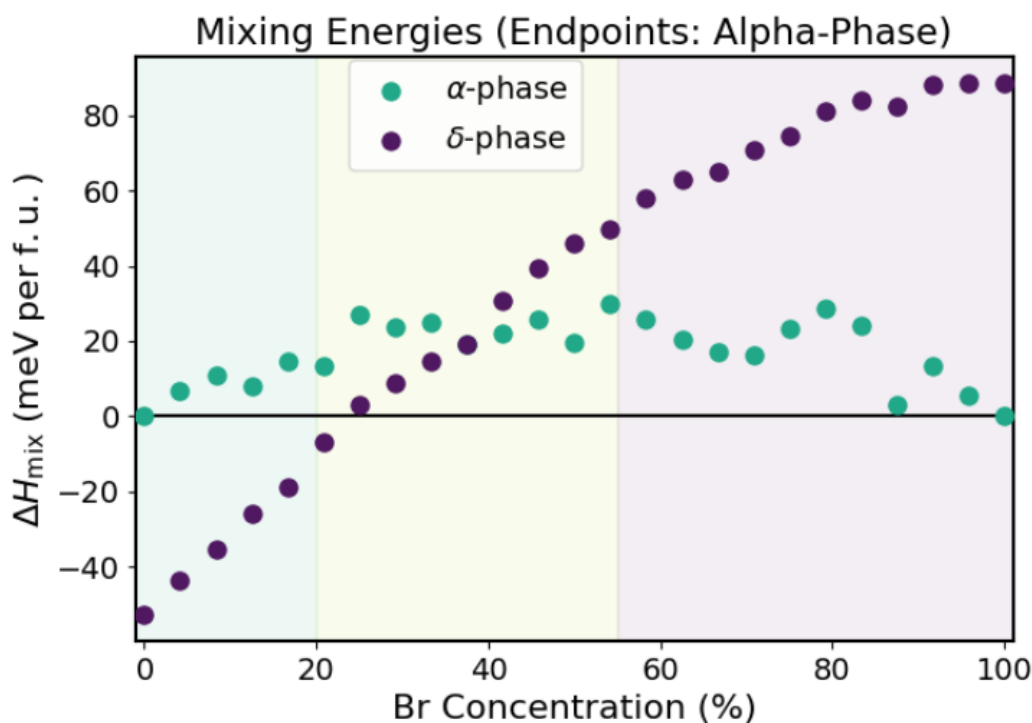


Figure 4.8: Comparison of the α - and δ -phase mixing energetics. Regions indicate preferential stability of each phase and the degeneracy region corresponding to the miscibility gap. The endpoints of the mixing enthalpy are set at 0 for the α -phase. Calculations were done by Tobias Loeff (Department of Materials, University of Oxford).

When the energetics of the δ -phase are compared with those of the α -phase in Figure 4.8, a clearer picture of the miscibility gap emerges. Since the entropic contributions arising from site disorder are equivalent for both phases, it is evident that the mixing enthalpies determine the relative phase stability. It is found that the δ -phase is more stable than the α -phase at lower Br

compositions ($< 20\%$), consistent with previous computational and experimental reports.^{15,69}

Experimentally, it has been shown that FAPbI_3 fabricated via one-step processing is only metastable at room temperature, in agreement with the model. Under ambient conditions, FAPbI_3 typically crystallises in the δ -phase. However, upon annealing at elevated temperatures ($\sim 150^\circ\text{C}$), the material can be driven into the α -phase. Despite this, the films gradually revert to the δ -phase when returned to room temperature under ambient conditions.¹⁵

For intermediate Br compositions ($\sim 20\% - 55\%$), the mixing enthalpies of the α - and δ -phases become nearly degenerate. In the absence of a significant kinetic driving force separating the two phases, the system experiences strong phase competition and both phases crystallise in the film. This explains the presence of the polytypes and the α -phase in the XRD pattern of the films fabricated in the previous section.

It is this near-degeneracy, rather than any intrinsic instability of the α -phase, that explains the emergence of the miscibility gap: a compositional region in which neither phase can crystallise uniformly because of competition between polymorphs (α vs. δ) at a fixed halide ratio. Although only the energetics of the δ -phase have been considered here to simplify the modelling, this framework can be extended to include other polytypes. In this context, phase competition is not limited to the α - and δ -phases, but may also involve additional polytypes present in the system.

The greater suppression of the α -phase in the centre of the miscibility gap, where a larger number of polytypes are observed, may therefore arise from increased competition between multiple polymorphs at specific compositions. This provides a consistent explanation for the experimental observations presented in the previous section. At higher Br contents ($> 55\%$), this situation reverses. Increasing Br incorporation stabilises the α -phase relative to the δ -phase, producing a clear free-energy separation that favours crystallisation of the photoactive phase.

If this degeneracy in the formation energies is responsible for the miscibility gap, then a strategy to circumvent this may exist. Researchers working with different materials, such as manganese oxides, have employed alternative kinetic pathways to favour the formation of selected polymorphs

over others in otherwise energetically competitive landscapes.⁶⁴ Similarly, in the following sections, various alternative crystallisation pathways are considered as a means to kinetically stabilise the α -phase in neat FA-based mixed-halide perovskites.

4.2.2 2-Step sequential deposition of perovskite using a lead halide template and an organohalide conversion

The first and simplest adjustment to the crystallisation pathway is to consider a two-step deposition of the perovskite. In a two-step deposition process, a $\text{PbI}_2/\text{PbBr}_2$ layer is first deposited from a DMF/DMSO solution. After annealing, the film is converted into a 3D perovskite by spin-coating an organohalide (FAI/FABr) onto the lead halide film. This processing route has been used in the literature to produce FAPbI_3 , among other compositions.⁷⁰ As there is no miscibility gap for the mixing of PbI_2 and PbBr_2 ,⁷¹ this should provide a viable starting point for the fabrication of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$. The composition of the films was controlled by matching the Br content in the template with that of the conversion solution. Figure 4.9 shows the XRD patterns of the two-step films.

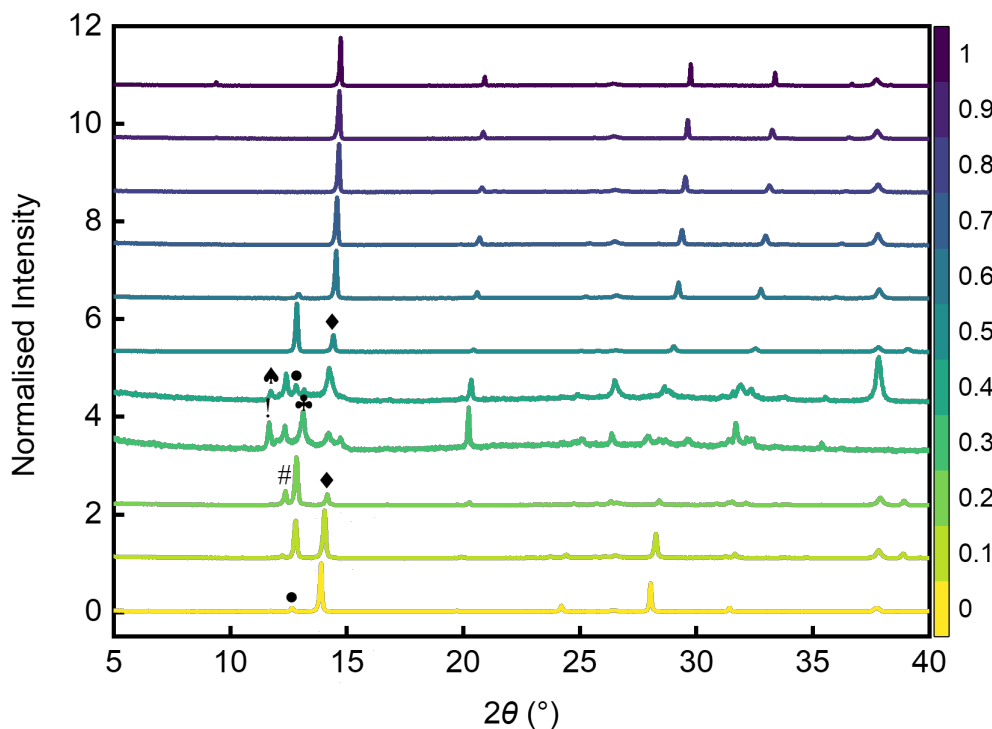


Figure 4.9: X-ray diffractograms of a series of 2-step $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. Normalised XRD patterns of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from DMF/DMSO via 2-step processing with increasing Br incorporation. From bottom (yellow pattern of FAPbI_3) to top (purple pattern of FAPbBr_3) in increasing increments of 10% Br. The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase, circle – (001) PbI_2 , spade – (100) 2H (δ -phase), club – (101) 4H, hashtag – (101) 6H, exclamation mark – (100) 4H.

Similar to the one-step films, different compositions exhibit varying numbers of phases within the region of interest between 11° and 15° . Some compositions, such as the 0% Br sample (FAPbI₃), exhibit only reflections corresponding to the (100) cubic α -phase (at 14°) and the (001) PbI₂ peak (at 12.7°). The 10% Br composition still shows a strong α -phase reflection; however, the PbI₂ reflection is significantly more intense. In addition, a small peak appears at 12.3° , which is not present in the 0% sample. This corresponds to the (101) reflection of the 6H phase³⁵, which was not observed in the one-step samples. The 20% Br composition exhibits the same phases as the 10% sample; however, the 6H reflection is more intense and the α -phase reflection is further suppressed. This differs from the one-step samples, where the 20% composition exhibited more than three phases. The greatest number of reflections is observed for the 30% and 40% Br compositions. In the 30% sample, in addition to the 6H and α -phase reflections, several additional peaks are present, corresponding to the (100) 4H reflection at 11.6° , the (100) 2H reflection at 11.8° , and the (101) 4H reflection at 13.2° . The (001) PbI₂ reflection is not observed in this composition. An additional peak at 14.7° , unique to this sample, could not be assigned to any known polytype reflection. For the 40% Br composition, all phases observed in the 30% sample remain, and the PbI₂ reflection reappears. For the 50% Br composition, only the α -phase and PbI₂ reflections are observed; however, the relative intensity of the PbI₂ reflection is greater than that of the α -phase. From 60% to 100% Br, the α -phase reflection is strong and no additional peaks are observed, consistent with the behaviour of the one-step films.

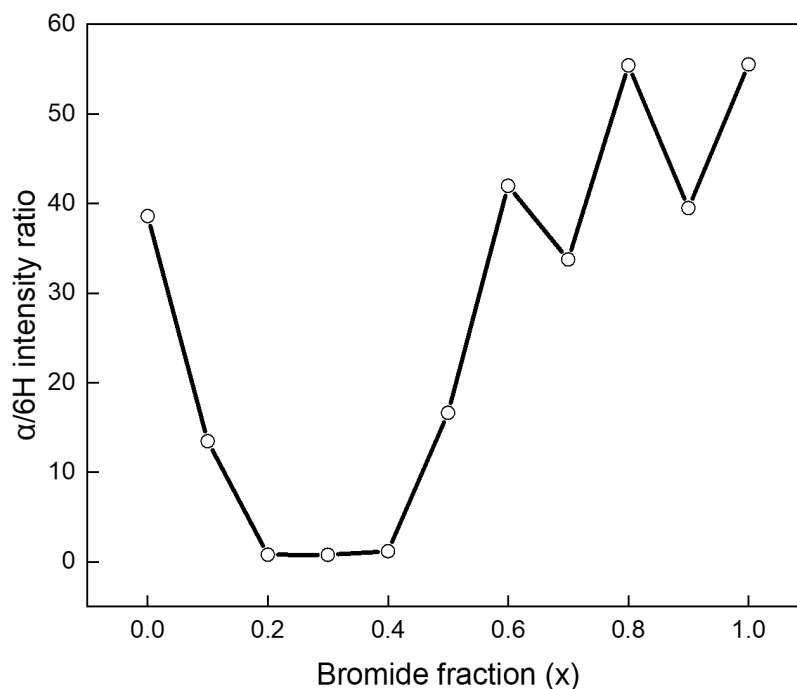


Figure 4.10: Relative intensity of (100) α - and (101) 6H phase reflections across a series of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. Relative intensity of α -phase and 6H phase plotted against bromide fraction (x) for $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films made via 2-step processing from DMF/DMSO. The peak position and integrated peak areas were calculated using a pseudo-Voigt fit.

To quantify the presence of polytypes relative to the α -phase across compositions, the relative phase fractions were estimated by comparing the integrated peak areas obtained from pseudo-Voigt fitting of the α -phase and 6H reflections. The resulting ratio is plotted as a function of composition in Figure 4.10. As the 6H phase was observed across the widest compositional range, it was selected as the reference for comparison. Comparing Figure 4.3 with Figure 4.10, it is evident that the α -phase fraction decreases relative to the polytype against which it is compared. However, the compositional range over which the α -phase is most suppressed is significantly narrower in the two-step films. In Figure 4.3, the region of greatest suppression spans from 10% to 60% bromide content, whereas in the two-step processed films this region is restricted to between 20% and 40% bromide. This suggests an improvement in the stabilisation of the α -phase resulting from the modified crystallisation pathway. It may indicate reduced phase competition at compositions outside the 20–40% range, allowing the α -phase to crystallise more readily in these regions.

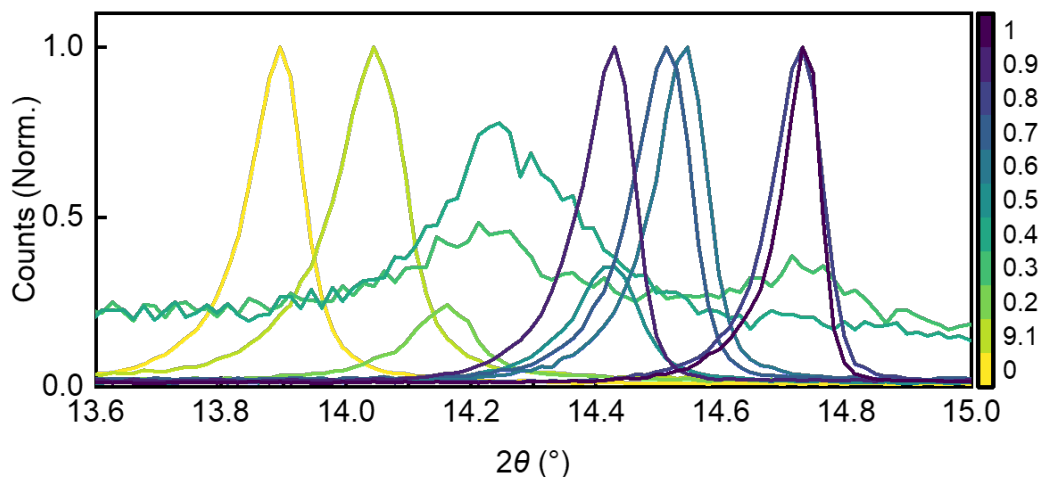


Figure 4.11: XRD patterns highlighting the α -phase reflection of 2-step $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. Normalised XRD patterns between 13.6° and 15° of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films made from DMF/DMSO via 2-step processing with increasing Br incorporation. From left (yellow pattern of FAPbI_3) to right (purple pattern of FAPbBr_3) in increasing increments of 10% Br.

The narrowing of the miscibility gap region is further supported by examining the profile of the (100) α -phase reflections. In Figure 4.11, a reduction in peak intensity accompanied by peak broadening is observed for compositions in the range $0.2 \leq x \leq 0.5$. This represents a narrower compositional window than that observed for the one-step films, which spanned $0.1 \leq x \leq 0.6$. The peak broadening is quantified in Figure 4.12, where the FWHM of the α -phase reflection is plotted across all compositions. The trend shows that the peaks remain sharp from 0% to 20% bromide, are broadest at 30%, and then become progressively sharper from 30% to 50%. From 50% to 100%, the peaks are as sharp as those of the 0% sample.

The combination of peak broadening and reduced α -phase intensity indicates increased structural disorder and reduced crystallinity, potentially associated with amorphous or poorly ordered regions. However, unlike the one-step films, significant peak broadening is observed only for the 30% and 40% compositions. This is consistent with the computational modelling, which suggests that competition between different phases is greatest for compositions in the centre of the miscibility gap. Consequently, crystallisation of the α -phase in these compositions is more challenging. However, the XRD data indicates that the miscibility gap has been narrowed, even if it has not been completely eliminated.

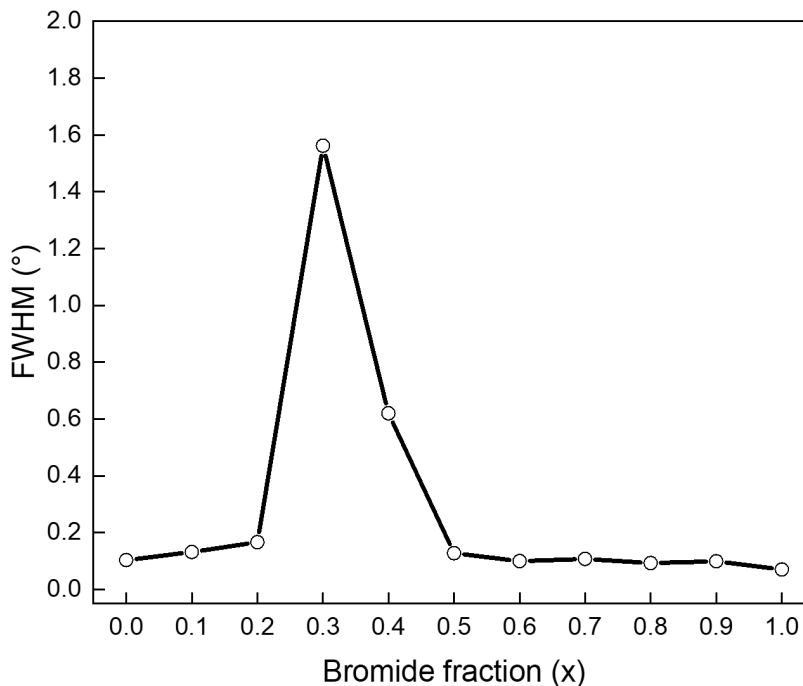


Figure 4.12: Full width at half maximum of (100) α -phase reflections across a series of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. FWHM of α -phase reflections across a series of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films plotted against the bromide fraction of the composition. The films were made via 2-step processing from DMF/DMSO. The FWHM was calculated using a pseudo-Voigt fit.

The UV-Vis spectroscopy measurements also support this claim. A sharp absorption onset is observed for both the 0% and 10% Br compositions, unlike in the one-step films, where the 10% composition exhibited a less well-defined onset. A slight loss of sharpness is observed for the 20% composition, while the 30% composition shows a significantly suppressed absorption onset. The 40% composition exhibits a profile similar to that of the 20% sample, with a moderately well-defined onset. The sharpness of the absorption onset is then recovered for compositions between 50% and 100% Br.

These observations are consistent with the conclusion that the miscibility gap region has been narrowed through two-step processing. Furthermore, they support the relationship between α -phase crystallinity and optical absorption, as the 30% composition, where the α -phase is most suppressed, also exhibits the weakest and least well-defined absorption profile. It also contains the greatest number of polytypes in its XRD profile. This reinforces the argument that the miscibility gap corresponds to a compositional region in which the α -phase crystallises poorly due to competition with other phases.

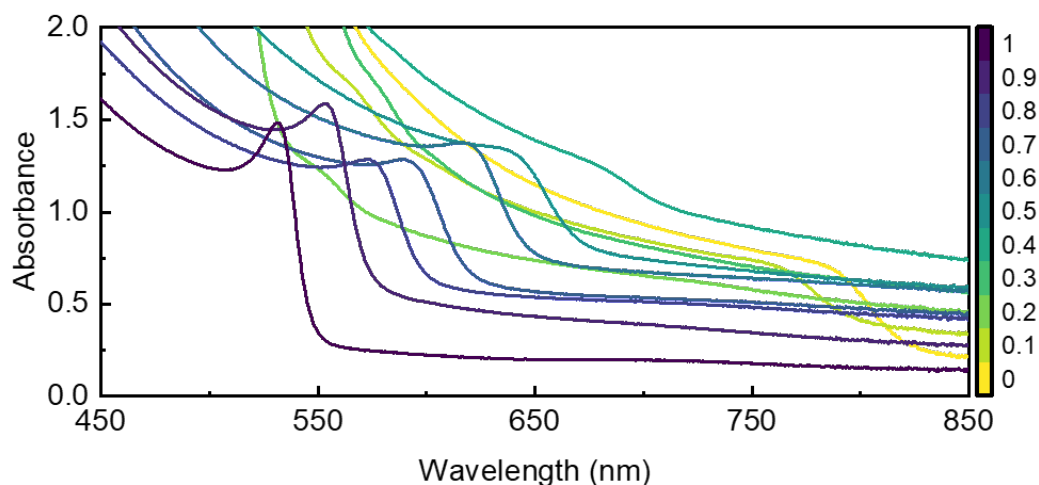


Figure 4.13: UV–Vis absorbance spectra of a series of 2-step $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. The films were prepared from DMF/DMSO via 2-step processing with increasing Br incorporation. From right (yellow pattern of FAPbI_3) to left (purple pattern of FAPbBr_3) in increasing increments of 10% Br.

4.2.3 MeTHF/BA

Another possible crystallisation pathway that may stabilise the perovskite is a two-step, 2D-templated topotactic deposition process.^{65,66} This has been shown to be an effective processing route for stabilising FAPbI_3 . As mentioned in the Theory section, FAPbI_3 exhibits intrinsic thermodynamic instability at room temperature, as the hexagonal δ - FAPbI_3 phase is thermodynamically favoured.¹⁵ However, this thermodynamic instability can be overcome through crystallisation pathways that kinetically stabilise the α -phase. Of particular relevance is previous work conducted by Gallant *et al.*⁶⁵ investigating the kinetic stabilisation of α -phase FAPbI_3 via a 2D templating approach. In that study, an $n = 2$ mixed BA/MA layered perovskite was first deposited and subsequently converted to α -phase FAPbI_3 by spin-coating a solution of FAI in butanol onto the template. This processing route produced films that were highly stable in the α -phase. Given that, in the case of FAPbI_3 , the competing phase is likewise a lower-symmetry δ -phase, this approach is likely to be promising for the kinetic stabilisation of mixed-halide compositions.

To incorporate Br^- into the films, the processing was adapted slightly from that used for the pure iodide composition. First, a mixed I/Br BA/MA $n = 2$ Ruddlesden–Popper template was fabricated, which was then converted by spin-coating an FAI/FABr solution onto the template. In this system, the precursor salts (MAI, MABr, PbI_2 , PbBr_2) were dissolved in 2-methyltetrahydrofuran

(MeTHF) and butylamine (BA), while FAI/FABr was dissolved in 1-butanol (BuOH). A schematic of the process is shown in figure 4.14.

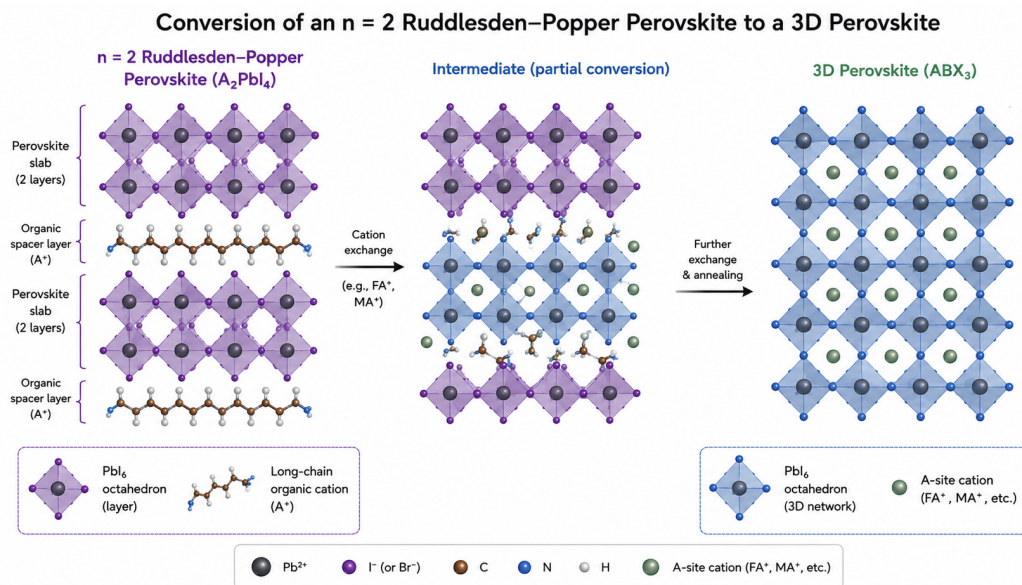


Figure 4.14: Schematic illustration of the conversion of an $n = 2$ Ruddlesden–Popper perovskite, comprising two perovskite slab layers separated by organic spacer layers, into a 3D perovskite. The process is shown as a sequence of cation exchange and annealing steps, passing through an intermediate partially converted state before yielding the final corner-sharing 3D ABX_3 framework. Purple and blue octahedra represent layered and 3D perovskite domains, respectively, while the organic spacer cations are progressively replaced by smaller A-site cations such as FA^+ or MA^+ .

The XRD patterns of these films are shown in Figure 4.15. Similar to the one-step and two-step films, a (100) α -phase reflection is observed across all compositions, along with a small PbI_2 peak. This indicates the presence of a crystalline α -phase in the films. However, there are few strong signals corresponding to polytypes within the miscibility gap region. Only weak 2H reflections are observed for the 50% and 60% compositions. This is more clearly illustrated in Figure 4.16, which compares the integrated peak areas of the α -phase and δ -phase.

It is apparent that the ratio of α -phase to δ -phase fractions decreases between the 30% and 70% Br compositions, as shown in Figure 4.16. However, the magnitude of this reduction is significantly smaller than that observed in the one-step and two-step films, where the α -phase is strongly suppressed across a wider compositional range. This indicates that, although polytypes are still present within this region, their relative phase fraction remains low compared to the α -phase. Furthermore, the reduced integrated peak areas and weaker reflections associated with the δ -phase suggest that these polytypes are less crystalline. Taken together, these observations

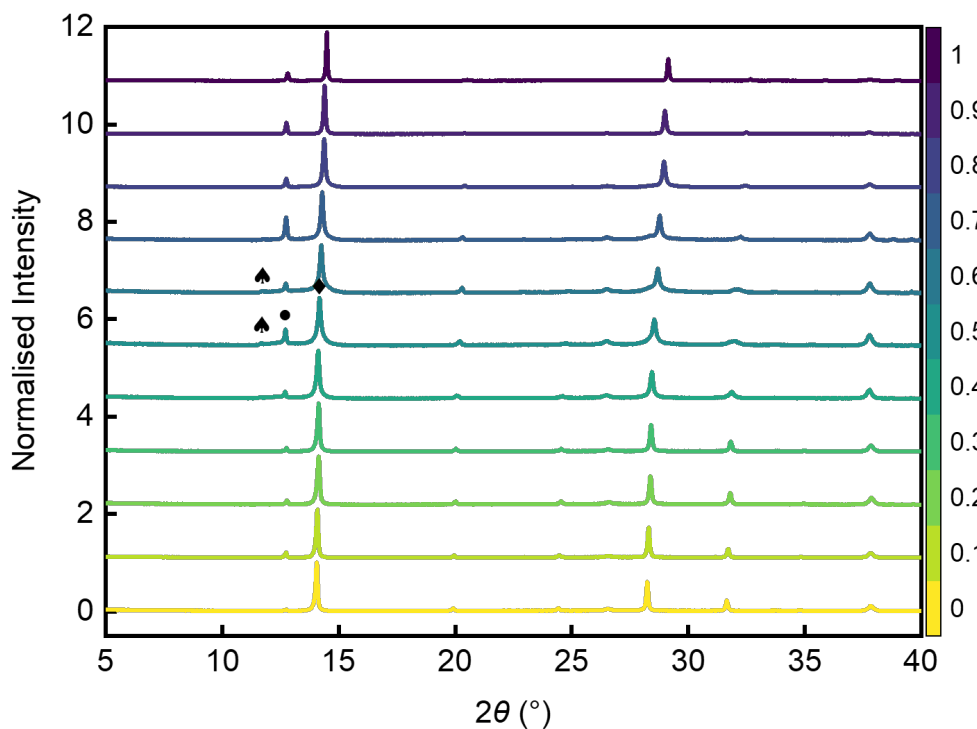


Figure 4.15: X-ray diffractograms of a series of MeTHF/BA $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. Normalised XRD patterns of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from MeTHF/BA via templated processing with increasing Br incorporation. From bottom (yellow pattern of FAPbI_3) to top (purple pattern of FAPbBr_3) in increasing increments of 10% Br. The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase, circle – (001) PbI_2 , spade – (100) 2H (δ -phase).

demonstrate that this processing route more effectively suppresses polytype formation and maintains a higher fraction of the α -phase across the compositional series.

Moreover, in the region of the (100) α -phase reflections (between 13.5° and 15°), shown in Figure 4.17, a consistent shift of the reflection towards higher angles is observed with increasing Br content in the films. This shift is indicative of lattice contraction and Br incorporation into the lattice.⁶⁰ The consistent presence of the α -phase reflection across the full compositional range supports the hypothesis that this crystallisation pathway facilitates the stabilisation of the α -phase and suppresses the formation of polytypes.

The FWHM of the α -phase reflections shown in Figure 4.18 further demonstrates that the films fabricated using MeTHF/BA exhibit sharper α -phase reflections compared to the one-step and two-step films. However, a slight peak broadening is observed for compositions between 30% and 70% Br. This corresponds to the compositional range in which the δ -phase exhibits a higher

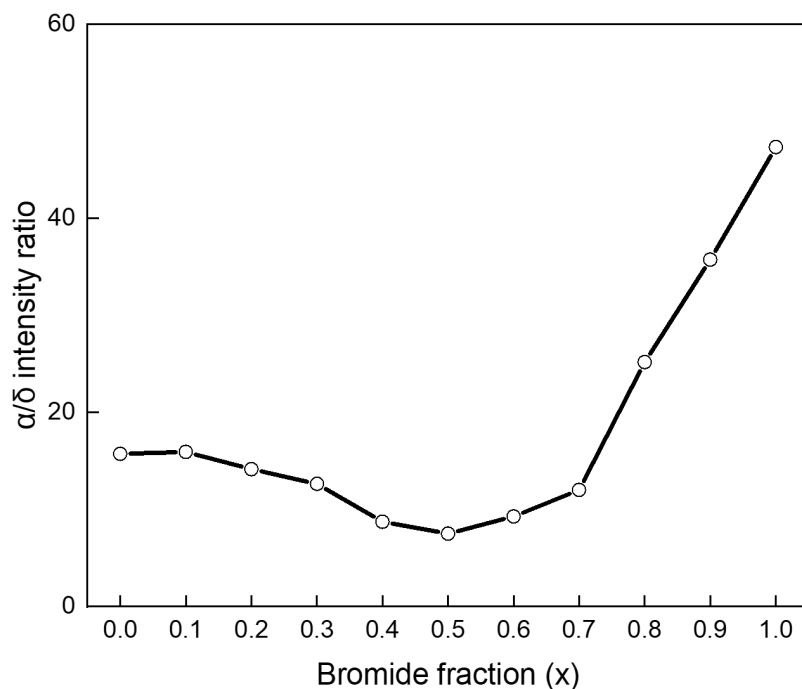


Figure 4.16: Relative intensity of (100) α - and (100) 2H phase reflections across a series of MeTHF/BA FAPb(I_{1-x}Br_x)₃ films. Relative intensity of α -phase and 2H phase plotted against bromide fraction (x) for FAPb(I_{1-x}Br_x)₃ films made via 2-step processing from MeTHF/NMP. The peak position and integrated peak areas were calculated using a pseudo-Voigt fit.

phase fraction in the XRD data. These observations support the hypothesis that the presence of polytypes in the film reduces the crystallinity of the α -phase.

The UV-Vis absorbance data shown in Figure 4.19 further confirm that the miscibility gap has not been completely eliminated in these films. A clear suppression of the absorption onset remains in the wavelength range between 670 nm and 770 nm, indicative of reduced crystallinity. In this system, the miscibility gap appears for compositions between 40% and 80% Br, which is consistent with the presence of polytypes observed in the XRD data and the reduced crystallinity of the α -phase. However, even within this suppressed region, the absorption onsets are visually sharper than those observed for the one-step (Figure 4.6) and two-step films (Figure 4.13). This is consistent with the reduced polytype content in the MeTHF/BA films and the relatively higher fraction of the photoactive α -phase.

The UV-Vis spectra also reveal several additional features of interest. It is apparent that the nominally 100% Br film does not correspond to a pure Br composition. FAPbBr₃ has a bandgap

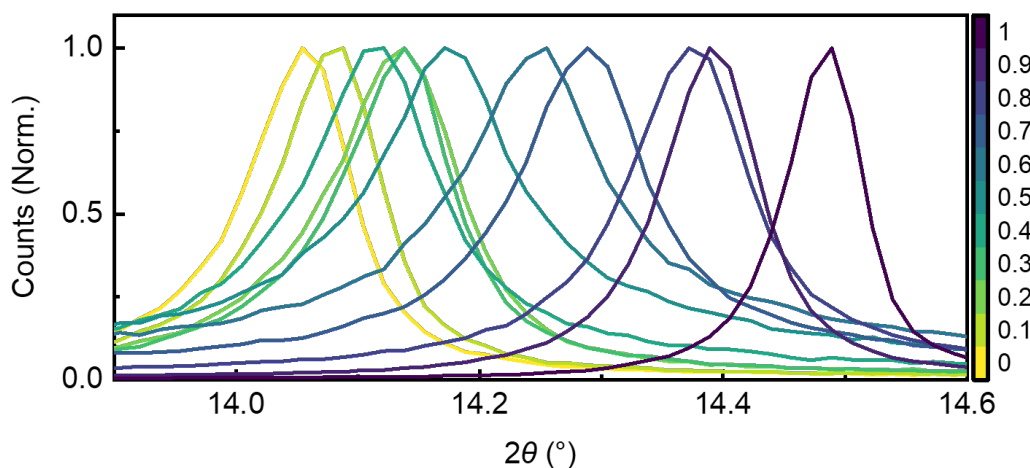


Figure 4.17: XRD patterns highlighting the α -phase reflection of MeTHF/BA FAPb(I_{1-x}Br_x)₃ films. Normalised XRD patterns between 13.5° and 15° of FAPb(I_{1-x}Br_x)₃ films prepared from MeTHF/BA via templated processing with increasing Br incorporation. Left (yellow pattern of FAPbI₃) to right (purple pattern of FAPbBr₃) in increasing increments of 10% Br.

of approximately 2.2 eV⁶⁰, corresponding to an absorption onset near 560 nm. In comparison with Figure 4.6, the absorption onset of the MeTHF-processed 100% Br film occurs at a longer wavelength (660 nm) than that of the control film prepared from DMF/NMP. This suggests that the MeTHF-processed film has a narrower bandgap than the reference FAPbBr₃ film. There is also a clustering of the absorption onsets for compositions on either side of the miscibility gap, indicating that they are not evenly spaced across the compositional range. Some compositions, such as the 60% and 70% Br films, even appear to overlap.

Taken together, these results demonstrate that this crystallisation pathway does not fully eliminate the miscibility gap. However, it does reduce the presence of polytypes in the films in the miscibility gap significantly. At the same time, there is a separate issue with the processing: the nominal content of the target compositions is not achieved in the final films.

The failure of this system to circumvent the miscibility gap may be attributed to limitations of the solvent system itself. In the original study conducted by Gallant *et al.*⁶⁵, MeTHF was selected due to its low boiling point and reduced toxicity compared with DMF. BA acted as a co-solvent and supplied the large BA⁺ cation required for formation of the 2D templates. It was shown that templates containing insufficient BA did not undergo successful conversion, owing to a lack of diffusion pathways for FA incorporation into the films, and therefore failed to stabilise FAPbI₃. Conversely, samples containing excess BA exhibited macroscopic cracking during conversion due

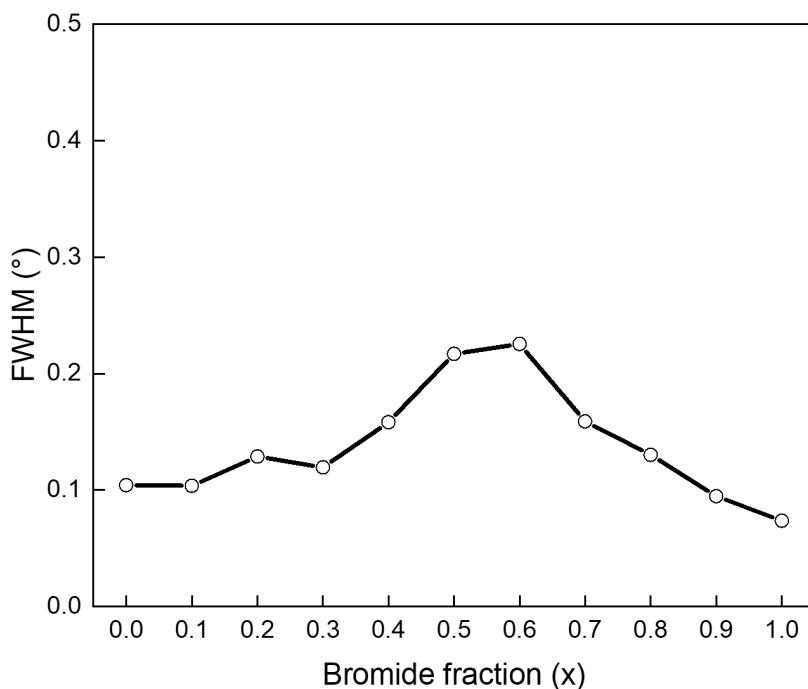


Figure 4.18: Full width at half maximum of (100) α -phase reflections across a series of MeTHF/BA FAPb(I_{1-x}Br_x)₃ films. FWHM of α -phase reflections across a series of FAPb(I_{1-x}Br_x)₃ films plotted against the bromide fraction of the composition. The films were made via MeTHF/BA 2-step processing from DMF/DMSO. The FWHM was calculated using a pseudo-Voigt fit.

to volume contraction upon expulsion of BA from the film. Ultimately, templates with $n \approx 2$ were found to be the most effective for crystallising FAPbI₃.

However, here, to incorporate more than $\sim 25\%$ bromide into the template, a greater proportion of BA solvent was used. This is not ideal because the amount of BA is critical in determining the n -value of the 2D templated film. Consequently, this has implications for both the conversion process and the morphology of the final 3D films. These constraints explain why films fabricated using this method did not span the entire range of compositions as intended. The processing was not optimised for the desired halide exchange to occur for all compositions. This could also potentially explain why the films still exhibited a miscibility gap. Because the Br content in the templates could not be independently tuned without simultaneously altering the BA concentration, different compositions had different n -values in the template. This likely compromises the conversion process, as each composition requires individual optimisation. This also reduces the generality of the method. Moreover, given that excessive BA adversely affects film morphology,

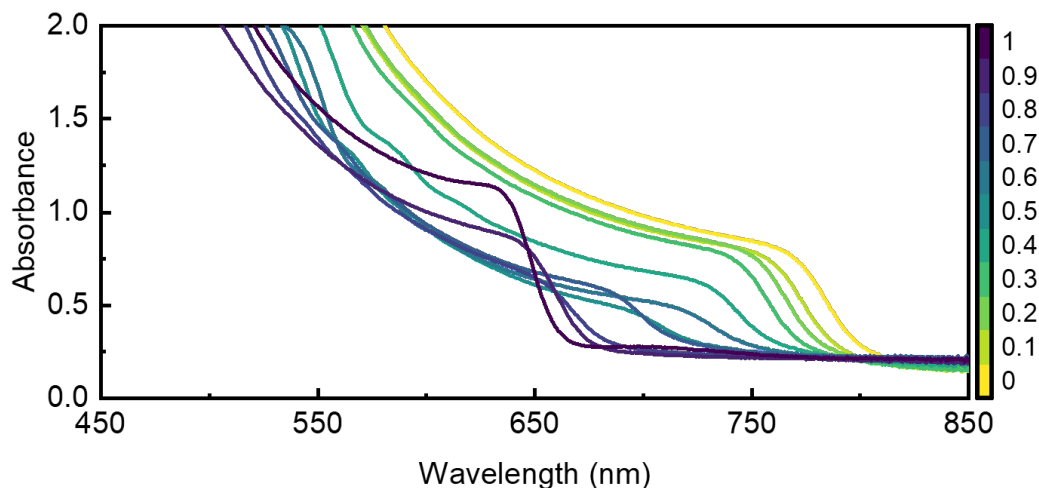


Figure 4.19: UV–Vis absorbance spectra of a series of MeTHF/BA $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. The films were prepared from MeTHF/BA via 2-step processing with increasing Br incorporation. Right (yellow pattern of FAPbI_3) to left (purple pattern of FAPbBr_3) in increasing increments of 10% Br.

fabrication of higher-bromide compositions is likely to be particularly challenging.

Given this, a change in solvent system is justified. If stabilisation of the α -phase is indeed driven by the formation of $n \approx 2$ templates, alternative solvent systems that are not limited by the poor solubility of bromide salts may be employed. In the next section, a DMF/NMP solvent system is used to fabricate suitable $n = 2$ Ruddlesden–Popper templates in an effort to eliminate the presence of polytypes from the films.

4.2.4 DMF/NMP

DMF/NMP solvent systems have been used for the fabrication of MHPs and are advantageous due to the excellent morphology of the resulting films and the degree of control they provide over phase crystallisation.⁷²

In this section, $n = 2$ BA/MA templates were fabricated using DMF/NMP rather than the MeTHF/BA system. The $\text{BA}_2\text{MAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$ templates were prepared by spin-coating a precursor ink containing salts dissolved in DMF/NMP, followed by gas quenching of the resulting films. As previous work demonstrated that stabilisation of FAPbI_3 relied on templates close to the $n = 2$ Ruddlesden–Popper (R–P) phase, such templates were reproduced for compositions containing 20% to 70% Br using the DMF/NMP system. This compositional range encompasses the miscibility gap as well as compositions on either side of it. The XRD patterns of these films are shown in Figure 4.20.

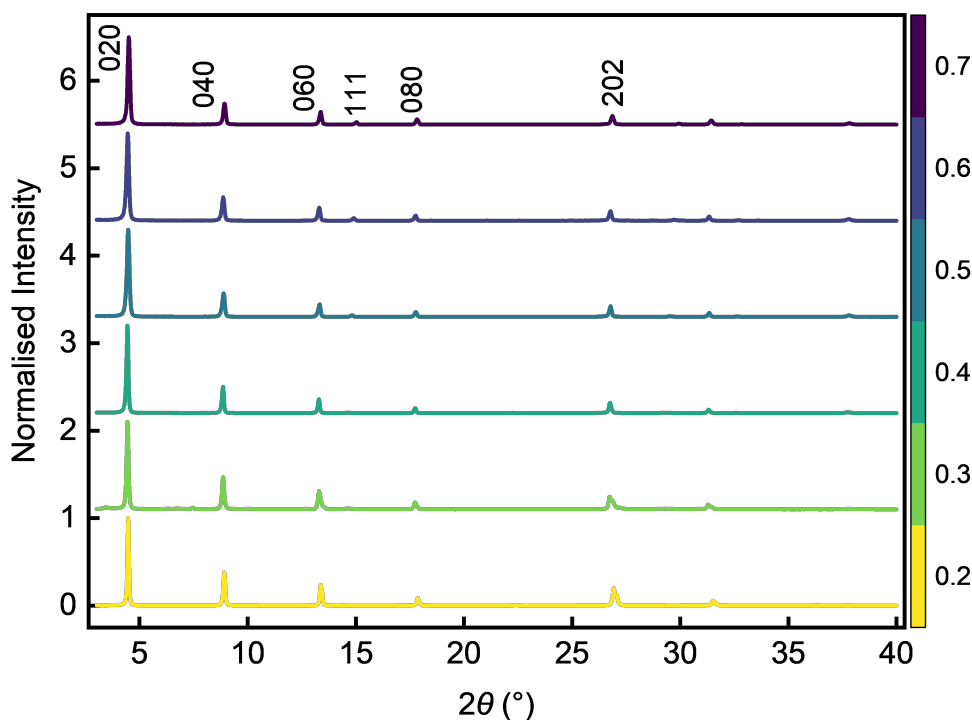


Figure 4.20: X-ray diffractograms of a series of $\text{BA}_2\text{MAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$ films. Normalised XRD patterns of $\text{BA}_2\text{MAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$ films prepared from DMF/NMP with increasing Br incorporation. From bottom (yellow pattern of FAPbI_3) to top (purple pattern of FAPbBr_3) in increasing increments of 10% Br. The reflections are consistent with previous reports by Stoumpos *et al.*

All samples exhibit reflections consistent with the $(02k0)$ series ($k = 1, 2, 3, \dots$), corresponding to the layered periodicity of $n = 2$ Ruddlesden–Popper perovskites.³² The first set of reflections

appears in the sub-5° region, as expected for the (020) plane. Additional higher-order reflections are observed at higher angles. In some samples, extra peaks are present, which can be assigned to in-plane perovskite reflections such as (111) and (202), in agreement with previous reports.³² These results indicate that the desired $n = 2$ phases were fabricated successfully. Images of the films shown in Figure 4.21 further demonstrate the highly specular morphology characteristic of gas-quenched films. Moreover, the progressive change in colour from red to yellow with increasing Br content is consistent with bandgap widening.

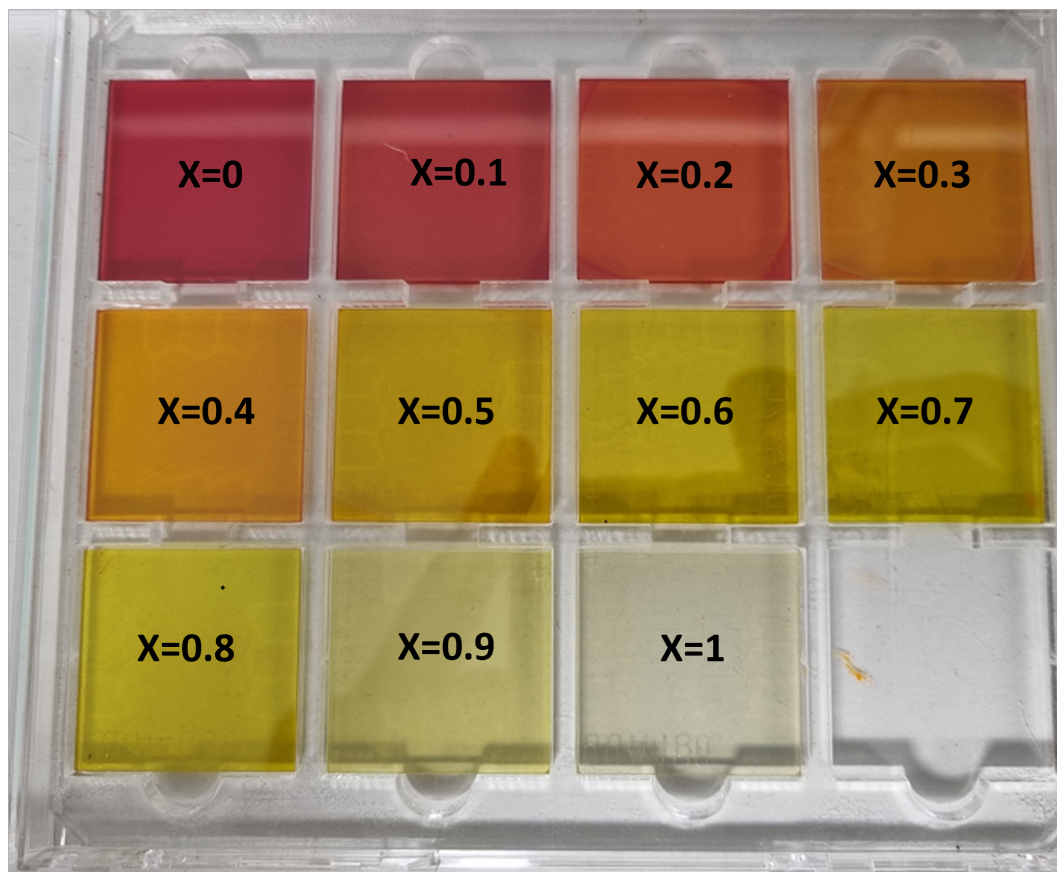


Figure 4.21: Photographs of $\text{BA}_2\text{MAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$ films prepared from DMF/NMP. Films are in order of increasing Br fraction (x) incorporation.

The templates were converted using the same procedure as in the MeTHF/BA system, involving treatment with an organohalide conversion solution followed by a high-temperature anneal to expel MA and BA from the final films. The XRD patterns of the resulting films are shown in Figure 4.22. Similar to the MeTHF/BA-derived films, the DMF/NMP films exhibit consistent, sharp α -phase reflections across the full compositional range. A further similarity between the two sets of films is observed in the region of the (100) α -phase reflection (between 13.5° and 15°), as shown in Figure 4.23, where the peak shifts to higher angles with increasing bromide incorporation. The α -phase reflection also has significantly lower intensity for the 30% to 60% compositions. However, unlike the MeTHF/BA films, no reflections indicative of polytype formation are observed in these samples.

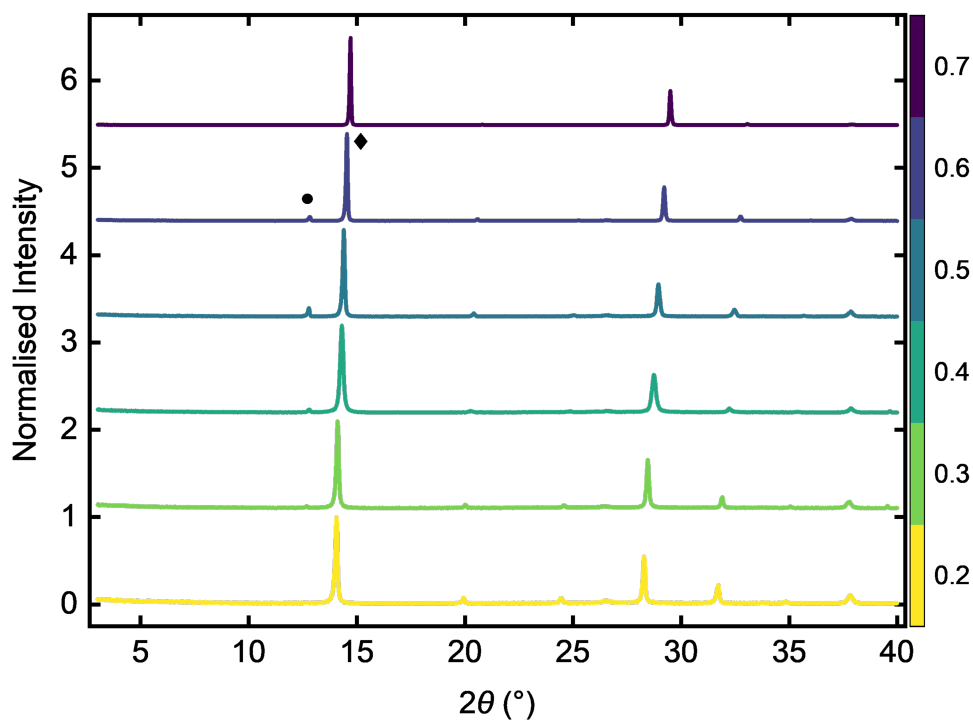


Figure 4.22: X-ray diffractograms of a series of templated $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. Normalised XRD patterns of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from DMF/NMP via templated processing with increasing Br incorporation. From bottom (yellow pattern of FAPbI_3) to top (purple pattern of FAPbBr_3) in increasing increments of 10% Br. The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase, circle – (001) PbI_2 .

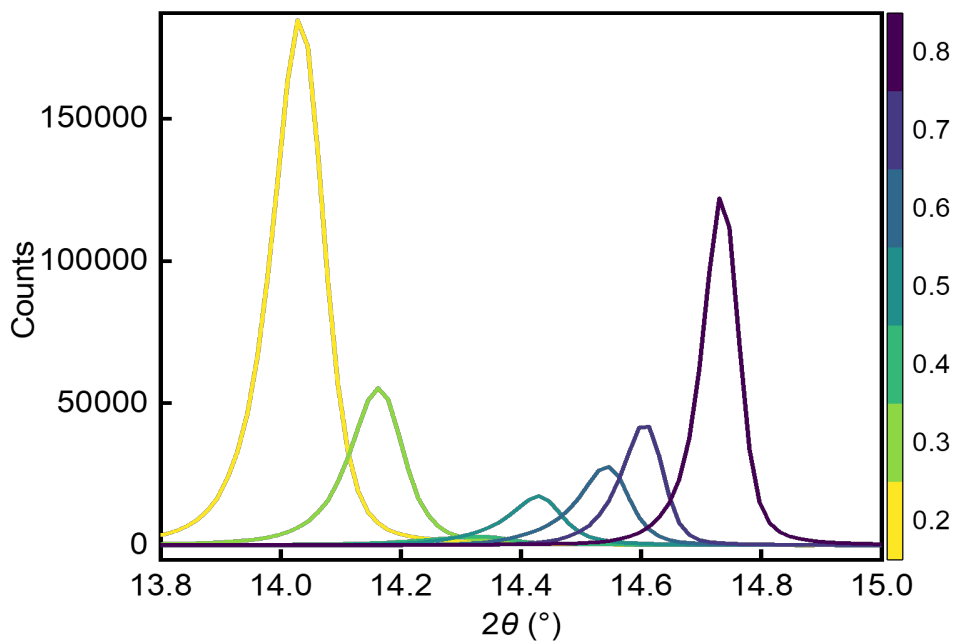


Figure 4.23: Unnormalised XRD patterns highlighting the α -phase reflection of 2-step templated $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. XRD patterns between 13.5° and 15° of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from DMF/NMP via templated processing with increasing Br incorporation. From left (yellow pattern of $\text{FAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$) to right (purple pattern of $\text{FAPb}(\text{I}_{0.3}\text{Br}_{0.7})_3$) in increasing increments of 10% Br.

The FWHM of the α -phase peaks is shown in Figure 4.24. The figure reinforces that this templated processing is successfully producing α -phase reflections across all compositions. Only the 40% composition exhibits a slightly broader peak.

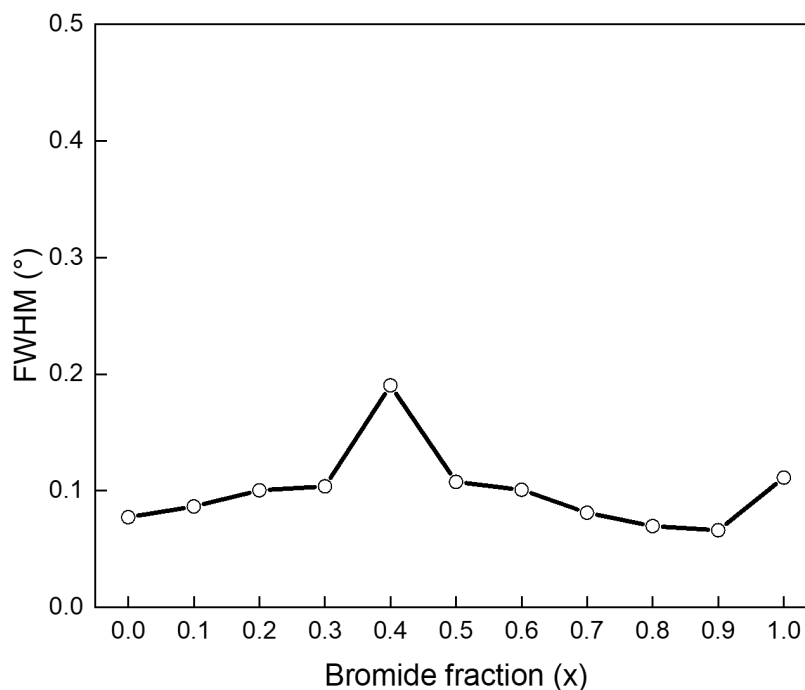


Figure 4.24: Full width at half maximum of (100) α -phase reflections across a series of 2D templated $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. FWHM of α -phase reflections across a series of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films plotted against the bromide fraction of the composition. The films were made via DMF/NMP 2-step processing from DMF/DMSO. The FWHM was calculated using a pseudo-Voigt fit.

Given the previous trend that reducing the presence of polytypes and having a more crystalline α -phase should result in sharp absorption profiles across all compositions, one might expect the films to exhibit consistently sharp absorption onsets. However, this is not what is observed in the UV-Vis absorption spectra shown in Figure 4.25. The 30% and 40% Br compositions exhibit significantly less well-defined absorption onsets than the other samples. In fact, these onsets are even less sharp than those observed for the MeTHF/BA films (Figure 4.19) and the two-step films (Figure 4.13). While the miscibility gap remains narrower than in the one-step films, the suppression of the absorption onset in the centre of the gap resembles that observed in the one-step case (Figure 4.6).

These observations suggest that simply eliminating polytypes and achieving consistently sharp α -phase reflections is insufficient to remove the miscibility gap. Instead, the reduced absorption

may indicate that films in the miscibility gap have poorer electronic order. This could arise from defects, strain, or local disorder associated with compositional inhomogeneity. This behaviour is observed specifically for the 30% and 40% compositions, which correspond to the region where the intensity of the α -phase reflection was lowest in Figure 4.23 and where modelling predicts the strongest competition between the α -phase and polytypes. Hence, in this case, the near-degeneracy of the Gibbs free energy between the competing phases does not lead to the formation of polytypes but may still result in a less electronically well-ordered material.

This poorer electronic order and reduced crystallinity may arise from incomplete conversion, leading to residual amorphous regions, or from lattice disruption during the cation-exchange process. Therefore, to promote complete conversion of the films into the α -phase, the next iteration of the method incorporates an intermediate annealing step.

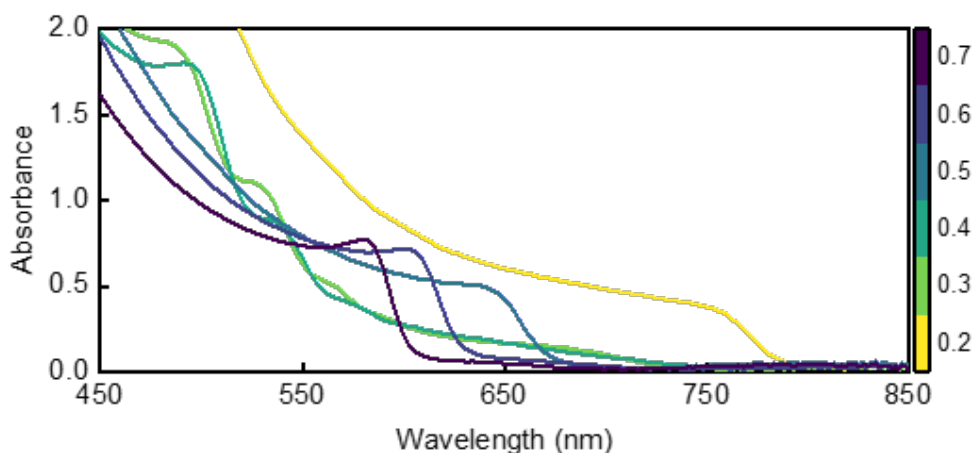


Figure 4.25: UV-Vis absorbance spectra of a series of 2D templated $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. UV-Vis absorbance spectra of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from DMF/NMP via templated processing with increasing Br incorporation. From right (yellow pattern of $\text{FAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$) to left (purple pattern of $\text{FAPb}(\text{I}_{0.2}\text{Br}_{0.8})_3$) in increasing increments of 10% Br.

4.2.5 DMF/NMP MA with anneal

As mentioned at the end of the previous section, one hypothesis for the inability of the DMF/NMP-templated films to eliminate the miscibility gap is that the templates may undergo incomplete conversion within this compositional region. The templating and conversion process is shown in Figure 4.26 and is briefly described here to aid understanding. To convert the 2D template, a solution of FAI/FABr is statically dispensed onto the substrate, allowing cation exchange to occur over a controlled time period before spin-coating. The BA spacer facilitates diffusion of FA^+ cations into the 2D material via interlayer channels. Consequently, cation exchange is expected to occur between FA^+ and the MA^+/BA^+ cations within the template.

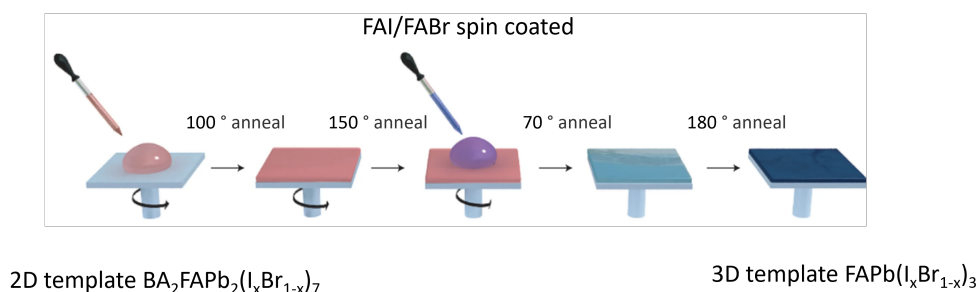


Figure 4.26: Schematic of film fabrication process with each annealing step indicated.

After spin-coating to remove excess conversion solution, the films undergo sequential thermal annealing: first at low temperature (70 °C for 10 minutes) and subsequently at high temperature (180 °C for 30 minutes). The high-temperature step is intended to drive out residual BA^+ and MA^+ , completing conversion to the 3D perovskite. To promote more complete conversion, an intermediate annealing step (150 °C for 15 minutes) was introduced to facilitate FA^+ interdiffusion. Films were fabricated across the compositional range and characterised using the same methods as in the previous section, with the addition of the intermediate anneal.

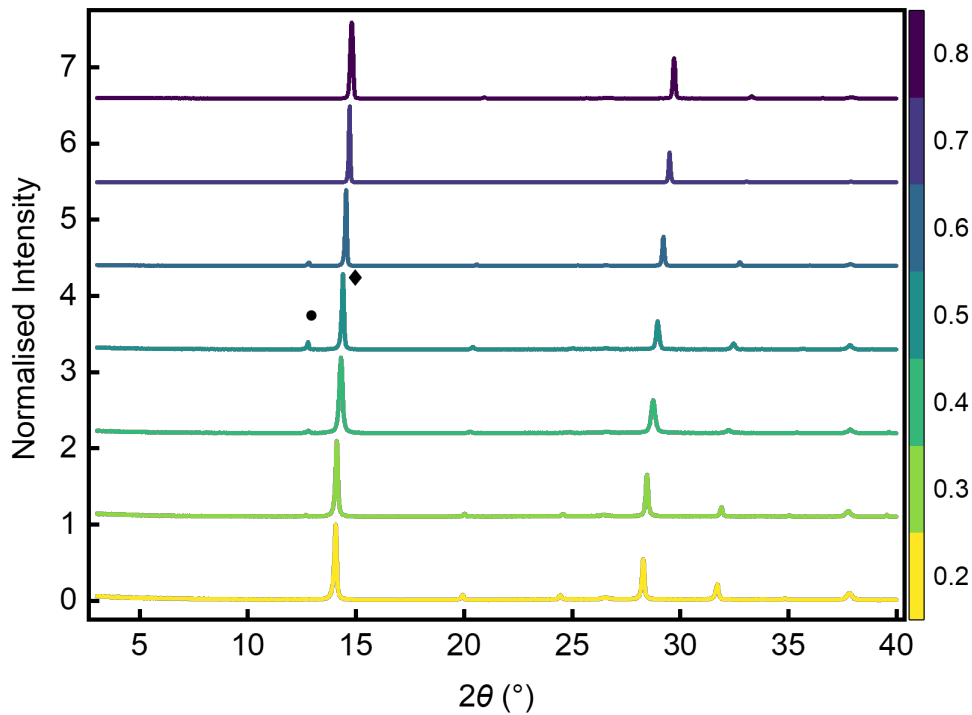


Figure 4.27: Normalised XRD patterns of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from DMF/NMP via templated processing with an intermediate anneal. Increasing Br from bottom (yellow pattern of $\text{FAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$) to top (purple pattern of $\text{FAPb}(\text{I}_{0.2}\text{Br}_{0.8})_3$) in increasing increments of 10% Br. The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase, circle – (001) PbI_2 .

The XRD patterns shown in Figure 4.27 exhibit a consistent set of reflections across the entire compositional range. Similarly, the (100) α -phase reflections shown in Figure 4.28 remain consistent throughout. These observations mirror those obtained for the DMF/NMP-derived 2D template films discussed previously, indicating the presence of crystalline α -phase perovskite in the films. The FWHM (Figure 4.29) of the α -phase reflections is also consistent across all compositions, suggesting that the α -phase has similar crystallinity across all films.

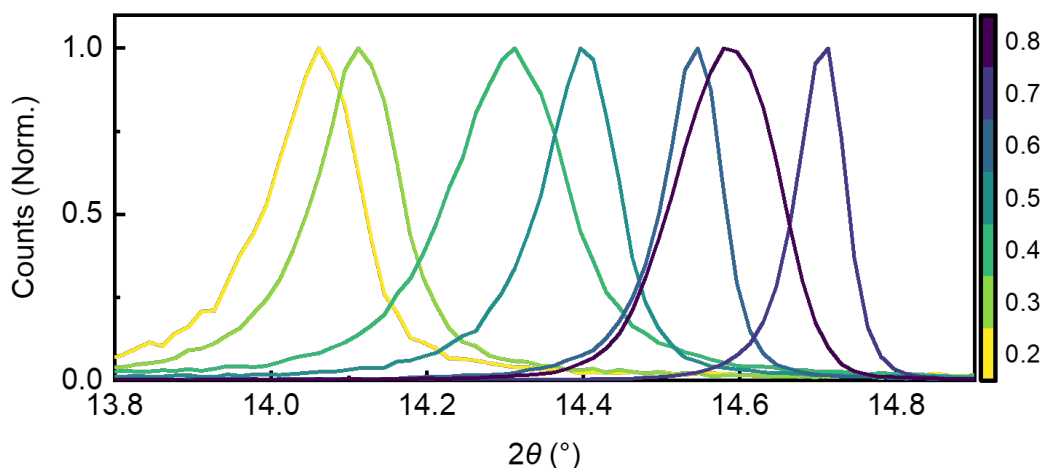


Figure 4.28: Normalised XRD patterns between 13.5° and 15° of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from DMF/NMP via templated processing with an intermediate anneal. Increasing Br from left (yellow pattern of $\text{FAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$) to right (purple pattern of $\text{FAPb}(\text{I}_{0.2}\text{Br}_{0.8})_3$) in increasing increments of 10% Br.

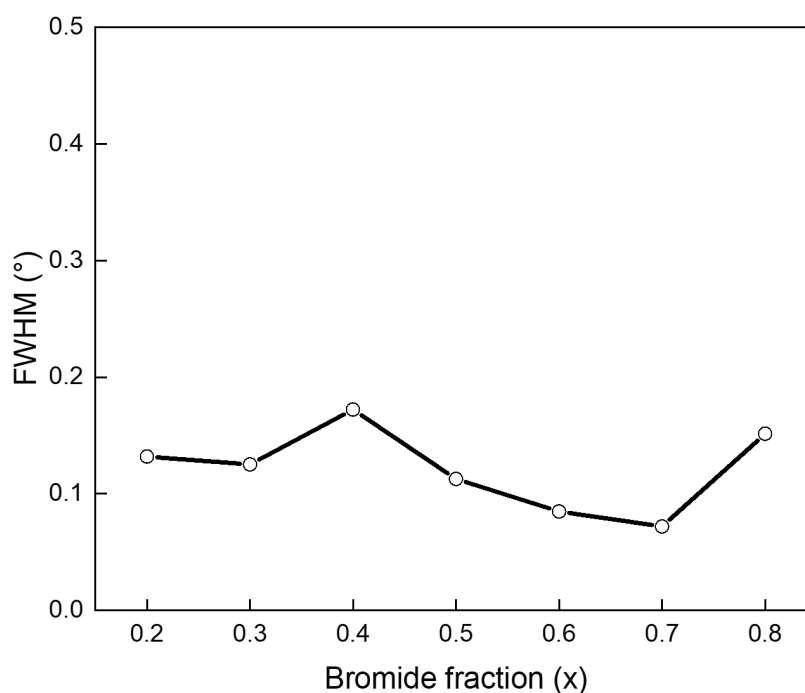


Figure 4.29: Full width at half maximum of (100) α -phase reflections across a series of intermediate annealed 2D templated $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films. FWHM of α -phase reflections across a series of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films plotted against the bromide fraction of the composition. The films were made via DMF/NMP 2-step templated processing with an intermediate anneal from DMF/NMP. The FWHM was calculated using a pseudo-Voigt fit.

However, unlike the previous processing method without the intermediate annealing step, the UV–

Vis absorbance spectra now exhibit clear and sharp absorption onsets at the expected bandgaps for each composition, as shown in Figure 4.30. This confirms the proposed hypothesis and demonstrates that incorporation of the intermediate annealing step within this templating approach enables the miscibility gap in $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskites to be circumvented.

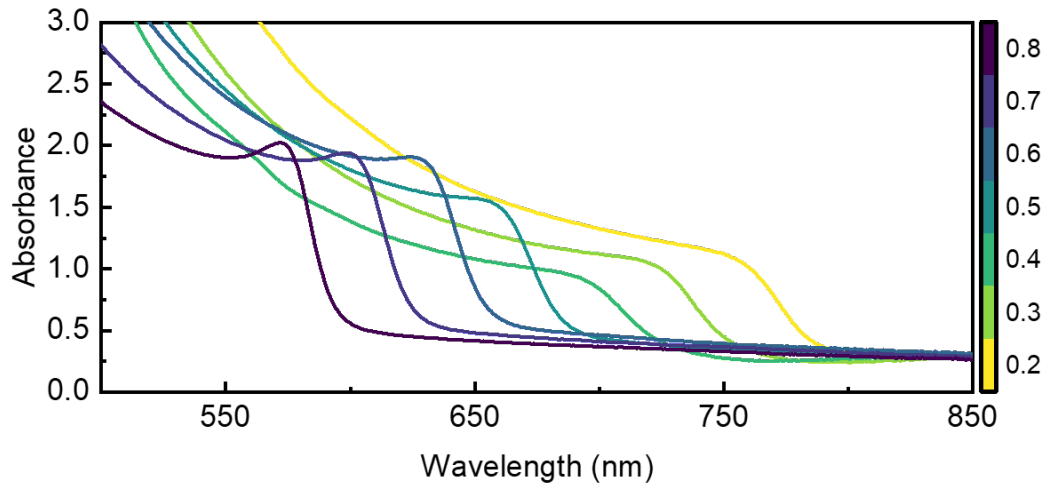


Figure 4.30: UV–Vis absorbance spectra of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from DMF/NMP via templated processing with an intermediate anneal. Increasing Br from right (yellow pattern of $\text{FAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$) to left (purple pattern of $\text{FAPb}(\text{I}_{0.2}\text{Br}_{0.8})_3$) in increasing increments of 10% Br.

To enable direct comparison between films processed with and without the intermediate annealing step, the diffractograms for both samples at the 30% Br composition are plotted together in Figure 4.31. This composition was selected because the degeneracy in formation energy between the α - and δ -phases is predicted to be most pronounced in this region. A photographic comparison of the two films is also provided in Figure 4.32.

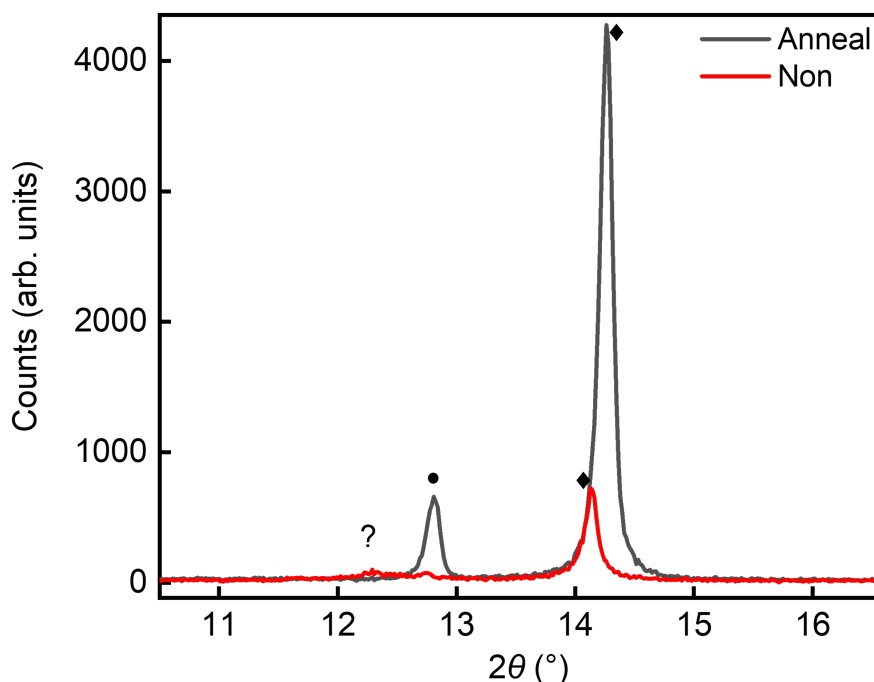


Figure 4.31: XRD patterns of $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films prepared from DMF/NMP via templated processing with and without an intermediate anneal. Red label: without anneal; black label: with anneal. The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase, circle – (001) PbI_2 , question – mark diffuse signal in the 2H region.

Both the control film, prepared without the intermediate annealing step, and the film subjected to intermediate annealing exhibit a reflection corresponding to the α -phase (100) plane. However, the control film shows significantly lower intensity than the intermediate-annealed film. The PbI_2 reflection is observed only in the intermediate-annealed samples. In addition, the non-intermediate-annealed films show a region of diffuse scattering around 11.7° , which could not be confidently assigned to a crystalline 2H phase and may instead indicate the presence of amorphous or poorly ordered material. Comparison of the photographs further highlights clear differences. The non-annealed films appear darker, less specular, and more transparent. The control films

also have visible pinholes. The lighter appearance and reduced specularly are consistent with the presence of amorphous material. Collectively, these observations indicate that the intermediate annealing step is essential for achieving complete conversion of the templated films and for stabilising the α -phase.

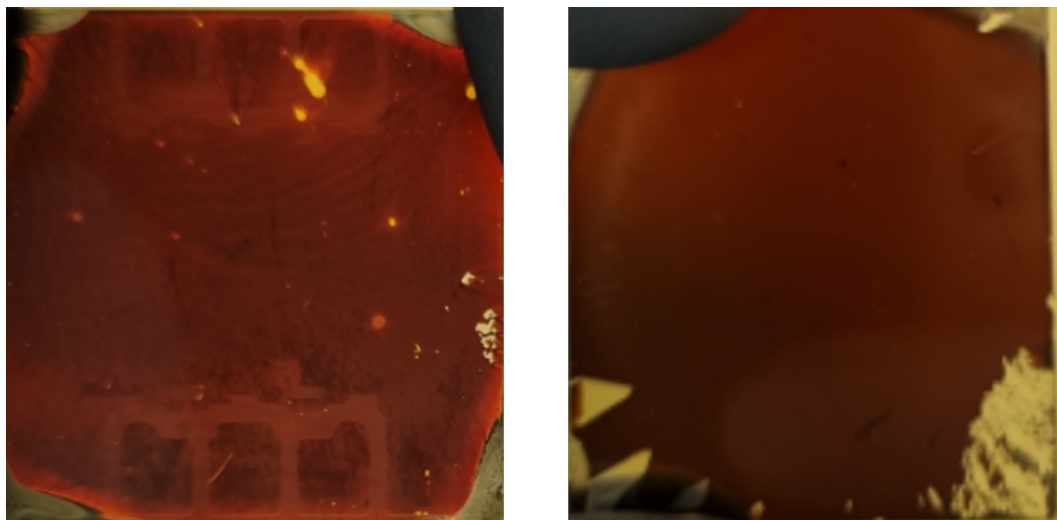


Figure 4.32: Photographic images of $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films prepared from DMF/NMP. Left: without intermediate anneal. Right: with intermediate anneal.

To further investigate the morphology of the films processed with the intermediate annealing step, scanning electron microscopy (SEM) images of the annealed films were acquired. The image reveals well-defined, compact grains without obvious morphological defects, such as pinholes. This provides additional evidence of the effectiveness of this processing method.

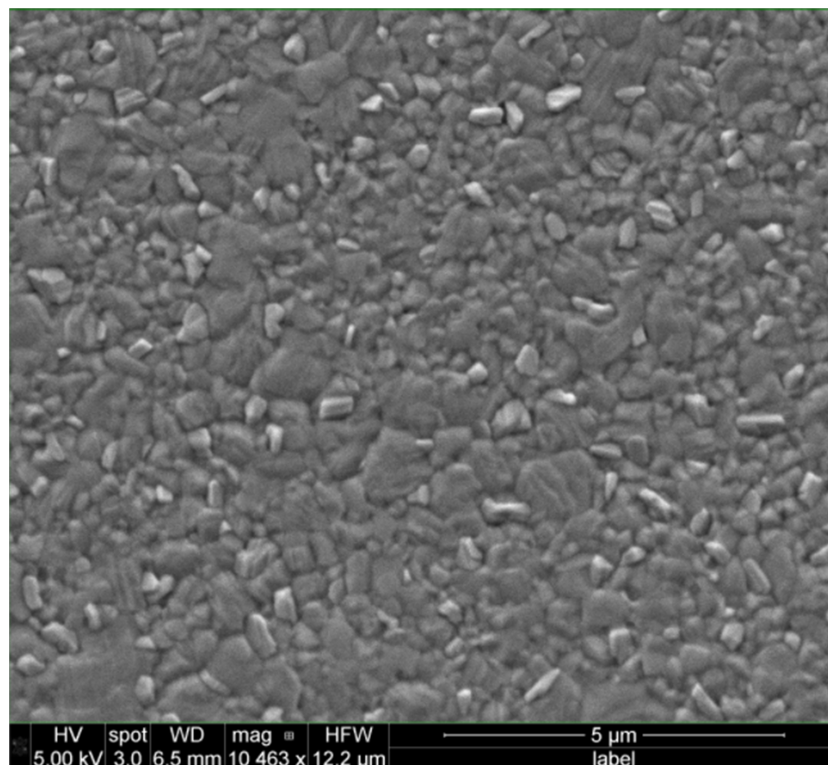


Figure 4.33: Scanning electron microscopy (SEM) image of a $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ film prepared from DMF/NMP with an intermediate anneal. The image shows compact grains without obvious morphological defects such as pinholes.

Although the importance of the intermediate annealing step has been demonstrated experimentally, the underlying mechanism remains unclear. To elucidate its role, computational simulations were performed in Figure 4.34. The modelling suggests that, at elevated temperature, the organic BA layer becomes more dynamic, creating transient pathways that facilitate diffusion of FA^+ into the structure. This enables replacement of BA^+ and MA^+ during the conversion process while preserving the integrity of the underlying mixed lead–halide octahedral framework.

Importantly, this thermal step does not disrupt the mixed-halide arrangement within the octahedra. Instead, it increases structural flexibility sufficiently to permit cation exchange while maintaining the lead–halide configuration established in the 2D phase. Therefore, the initial hypothesis was partially correct. The intermediate annealing step does indeed facilitate the conversion process by opening diffusion pathways within the templated structure. However, the computational model provides additional insight: elevated temperature enables retention of the

lead–halide octahedral network from the 2D perovskite in the final film. This preservation of the octahedral framework ultimately completes the stabilisation of the α -phase.

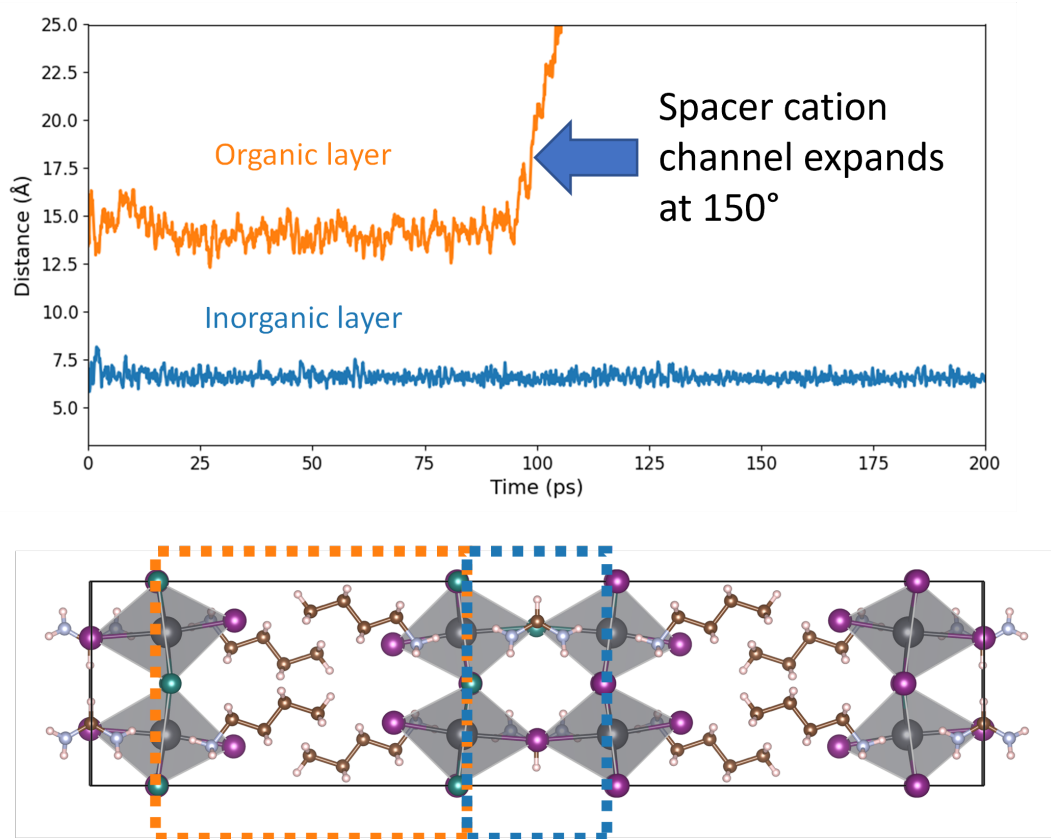


Figure 4.34: Molecular dynamics of 30% Br 2D perovskite at 520 K. The organic (orange) and inorganic (blue) layers are defined by the Pb–Pb atom distances as shown in the structure at the bottom of the figure. Calculation was done by Tobias Loeff (Department of Materials, University of Oxford).

Despite the apparent success of this method, alternative explanations for the elimination of the miscibility gap must also be considered. Notably, the presence of MA in the templated layer raises the possibility that residual MA may remain in the final film, thereby contributing to stabilisation of the α -phase. Mixed FA/MA perovskites are known to readily crystallise into the α -phase via conventional one-step processing. If this were the case, the final films would not be FA-pure but instead mixed FA/MA perovskites.

To assess the presence of MA in the converted films, proton nuclear magnetic resonance (^1H NMR) measurements were performed to quantify the MA content in the final films. The spectra for both the 2D templates and the converted films are shown in Figure 4.35. The results confirm that the templates contain MA, as evidenced by prominent signals corresponding to the methyl (CH_3) and

ammonium (NH_3^+) groups of MA. After conversion, signals corresponding to the methine (CH) and amine (NH_2) groups of formamidinium confirm the presence of FA in the films. However, the converted films also exhibit residual signals corresponding to the MA methyl group, indicating that a non-negligible amount of MA remains. This suggests that the final films are not purely FA-based perovskites.

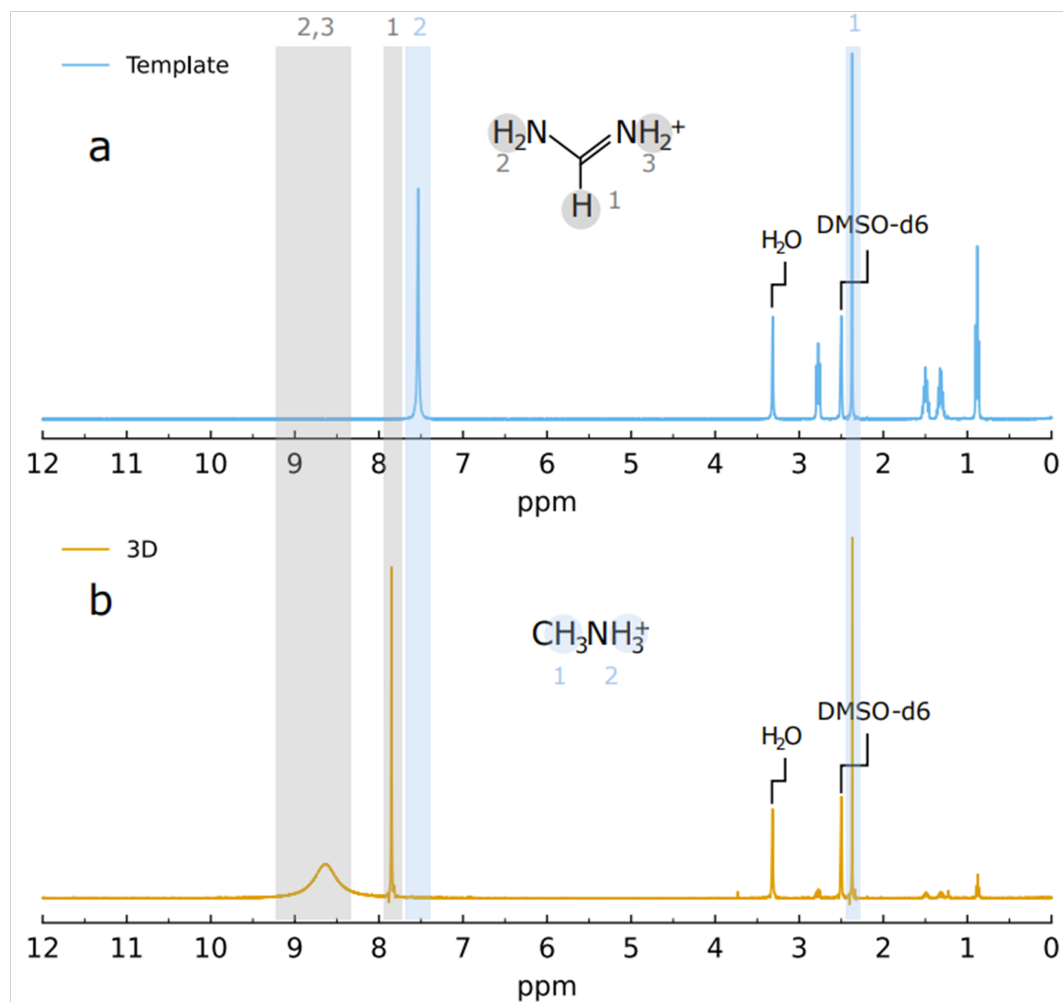


Figure 4.35: Solution ^1H NMR spectra of a $\text{BA}_2\text{MAPb}_2(\text{I}_{0.7}\text{Br}_{0.3})_7$ template layer and converted $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$. The main peaks can be attributed to the protons of the methine [CH (1)] and amine [NH_2 (2, 3)] groups of formamidinium highlighted in grey and the protons of the methyl [CH_3 (1)] and ammonia groups [NH_3 (2)] of methylammonium highlighted in blue. Measurements were taken by Siyu Yan (Department of Physics, University of Oxford).

4.2 CONCLUSION

In this chapter, the presence of the miscibility gap has been reproduced, corroborating previous reports in the literature.^{60,61} Furthermore, this work has advanced the understanding of the miscibility gap by linking the reduced crystallinity of the α -phase to the presence of polytypes within the films. This observation has led to a proposed explanation for the origin of the miscibility gap through novel applications of machine-learning interatomic potentials. This model builds on recent work that has challenged the prevailing view that the miscibility gap arises from an intrinsic thermodynamic instability of the α -phase at certain halide compositions in FA-based perovskites. Instead, the present model attributes the miscibility gap to a near-degeneracy in the Gibbs free energy of the α - and δ -phases (which is extended to other polytypes more generally) for halide compositions between 20% and 60% Br content. This results in films with reduced α -phase crystallinity and the formation of non-photoactive polytypes.

This framework accounts for the full range of experimental observations associated with the miscibility gap, including its presence in FA-based but not MA-based perovskites, the prevalence of the δ -phase below 20% Br content, the specific compositional window in which the gap is observed, and the dominance of the α -phase at compositions exceeding 60% Br content.

Various crystallisation pathways were subsequently explored in an effort to circumvent the miscibility gap, including conventional two-step processing and 2D-templated deposition. Conventional two-step processing proved unsuccessful, as polytypes were still observed in the films, suggesting that miscibility of the lead halides alone is insufficient to eliminate their presence in the final films. However, the compositional range over which the miscibility gap was observed was narrowed to approximately the 30%–40% Br compositions.

The MeTHF/BA films further improved upon the two-step processing by reducing the presence of polytypes, with only the 2H phase detected in the 50% and 60% compositions. This was also reflected in an improvement in the absorption onset for these films. Furthermore, templates fabricated using the MeTHF/BA solvent system were limited by the poor solubility of bromide salts,

preventing the development of a general processing route across all compositions. To address this limitation, a DMF/NMP solvent system was employed for template fabrication. While initial attempts were again unsuccessful in fully stabilising the α -phase, XRD patterns indicated the presence of crystalline α -phase material. However, the absence of sharp absorption onsets in the UV–Vis spectra suggested that amorphous material remained within the films. This elucidated on another aspect of the miscibility gap, namely, that simply removing polytypes from the films is not sufficient to have a highly crystalline α -phase. It was proposed that the films can still be a mixture of amorphous and crystalline material due to the incomplete conversion.

To promote more complete conversion, an intermediate annealing step was introduced. This modification yielded encouraging results, with both UV–Vis and XRD measurements indicating that the films were predominantly composed of α -phase perovskite. Nevertheless, NMR analysis revealed that the final 3D films were not purely FA-based, as residual MA from the template remained incorporated within the structure.

To address this limitation, the next chapter investigates the use of FA-based templates in an effort to eliminate MA incorporation and achieve phase-pure FA perovskite films.

CHARACTERISATION OF TEMPLATED $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$

5

5.1 INTRODUCTION

In the preceding chapter, the viability of using 2D-templated perovskites to circumvent the miscibility gap was explored. However, the presence of methylammonium (MA) in the converted films suggested that they were not neat formamidinium (FA) perovskites. This is problematic for two reasons. Firstly, the miscibility gap is known not to exist in mixed FA/MA lead halide perovskites, making the claim of circumventing the miscibility gap questionable.⁷³ Secondly, MA-containing perovskites are less thermally stable than FA-based perovskites, as MA can leave the film as methylamine gas under thermal stress.⁷⁴ Therefore, in this chapter, FA Ruddlesden–Popper (R–P) templates were used instead of MA templates, thereby eliminating MA from the process altogether.

The first challenge was to identify a solvent system and quenching method capable of producing films with specular morphology and conformal coverage while crystallising the correct phase. It was found that this was best achieved using the same DMF/NMP solvent system as before, in conjunction with a diethyl ether (DEE) anti-solvent quench rather than a gas quench. The templates were then verified by XRD to have crystallised in the correct $n = 2$ R–P phase. Subsequently, the templates were converted to the 3D phase using the same process as for the MA templates, and it was confirmed using XRD and UV–Vis spectroscopy that the α -FAPb(I_{1-x}Br_x)₃ phase was stabilised across the full compositional range from pure iodide to bromide. However, cross-sectional SEM measurements revealed delamination at the bottom interface. This issue was resolved by reducing the BA content in the templates. Films prepared from the modified templates were again characterised by UV–Vis and XRD, confirming that this processing route also circumvented the miscibility gap.

To explain the success of this crystallisation pathway in circumventing the miscibility gap, computational modelling was employed. The models suggested that the 2D phase does not exhibit a miscibility gap and can therefore act as a crystallisation pathway for the α -phase.

In the final part of the chapter, the optoelectronic properties of the 30% Br composition were characterised using a range of spectroscopic techniques. Finally, the 30% Br composition was incorporated into photovoltaic devices, and their performance was evaluated.

5.2 RESULTS AND DISCUSSION

5.2.1 Optimisation of processing

To produce FA-based templates, the MA salts in the precursor solution were replaced with FA salts. However, this modification introduced significant challenges in controlling film morphology. FA-rich and MA-rich precursor inks exhibit different crystallisation kinetics, with MA-based perovskites generally crystallising more rapidly.⁷⁵ Consequently, a quenching protocol that is effective for MA-based systems does not directly translate to FA-based systems, often resulting in markedly different film morphologies. The key challenge, therefore, was to develop a quenching strategy suitable for $n = 2$ FA-based Ruddlesden–Popper (R–P) templates that could reliably produce specular, uniform films with conformal coverage.

The first approach was to use a gas quenching method, akin to the MA case. A photograph of the gas-quenched $\text{BA}_2\text{FAPb}_2\text{I}_7$ template is shown in Figure 5.1(a). It is clear from the photograph that the films are rough, as evidenced by the haziness of the surface. The films are not uniform either, with different regions showing features such as streaks or swirling patterns. It was observed that the films crystallised in stages during gas quenching. The portion of the film directly under the gas quenching pipe crystallised faster than other areas. The circular pattern in the centre of the image illustrates this effect.

The lack of success in gas quenching was not unexpected, given the aforementioned concerns when substituting MA with FA. Therefore, other common anti-solvents were chosen to improve the processing⁷⁶, including anisole, methyl acetate, and diethyl ether (DEE). The resulting $\text{BA}_2\text{FAPb}_2\text{I}_7$ films are shown in Figure 5.1(b–d), respectively. The anisole and methyl acetate films show similar haziness (due to a rough top surface) as the gas-quenched films. However, they do exhibit improved uniformity, particularly for the film quenched with anisole. The DEE films are highly specular and uniform, suggesting that this is the most suitable processing method.

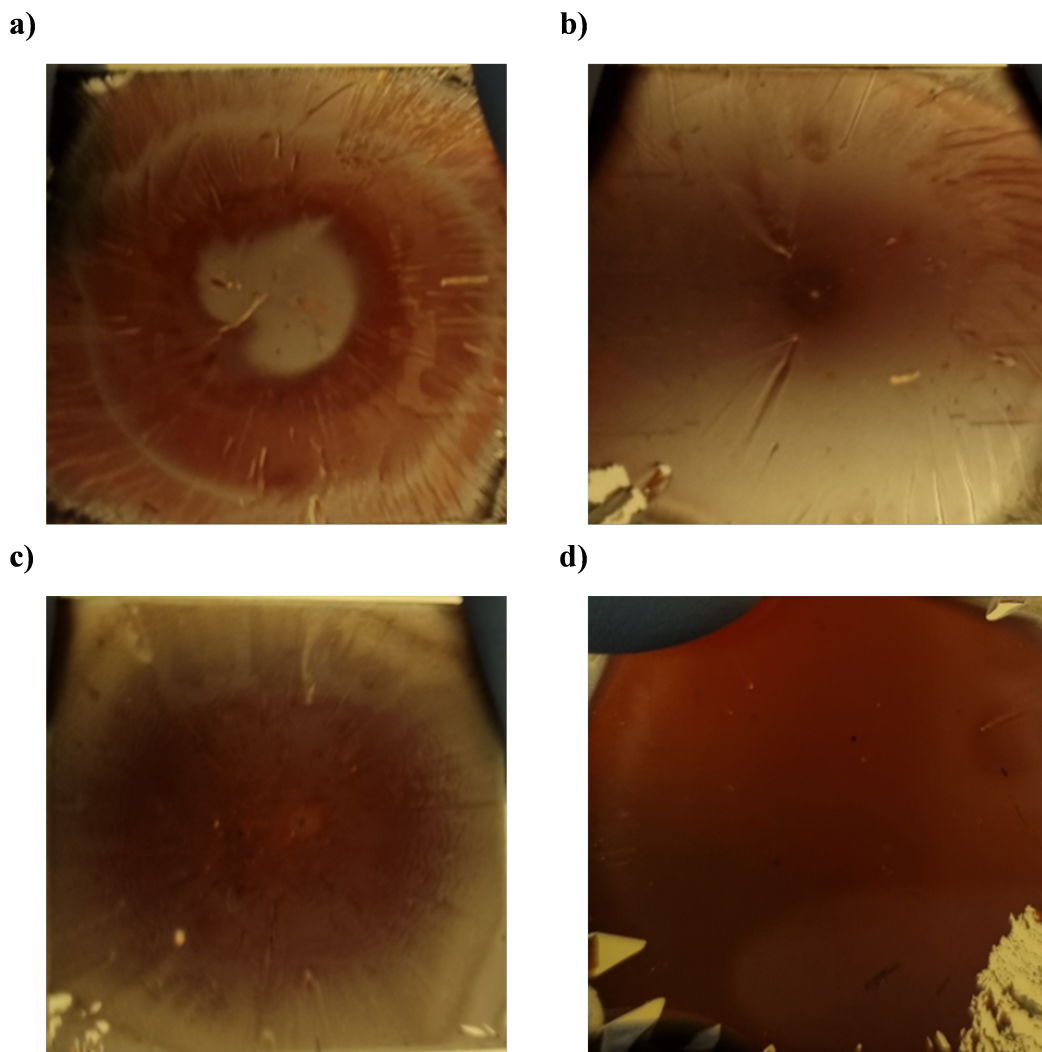


Figure 5.1: Photographs of $\text{BA}_2\text{FAPb}_2\text{I}_7$ films prepared from DMF/NMP. Films were prepared using: (a) a gas quenching method, (b) $325\ \mu\text{L}$ of anisole for the anti-solvent quench, (c) $325\ \mu\text{L}$ of methyl acetate for the anti-solvent quench, and (d) $800\ \mu\text{L}$ of diethyl ether for the anti-solvent quench.

Having addressed the morphological issues of the FA templates, XRD measurements were performed to verify whether the targeted $n = 2$ Ruddlesden–Popper (R–P) phase had crystallised. Films spanning compositions from 20% to 50% bromide were examined, and the corresponding diffractograms are shown in Figure 5.2. The observed reflections are consistent with the $(0, 2k, 0)$ family of reflections (k being an integer representing higher-order reflections) characteristic of $n = 2$ R–P perovskites. As expected, the first set of reflections appears in the sub- 5° region, in good agreement with previously reported data.^{32,77} The presence and systematic evolution of these reflections across the compositional range indicate that the desired $n = 2$ R–P phases were successfully crystallised for compositions relevant to the miscibility gap.

Having established that the templates had crystallised in the desired phase, the next step was

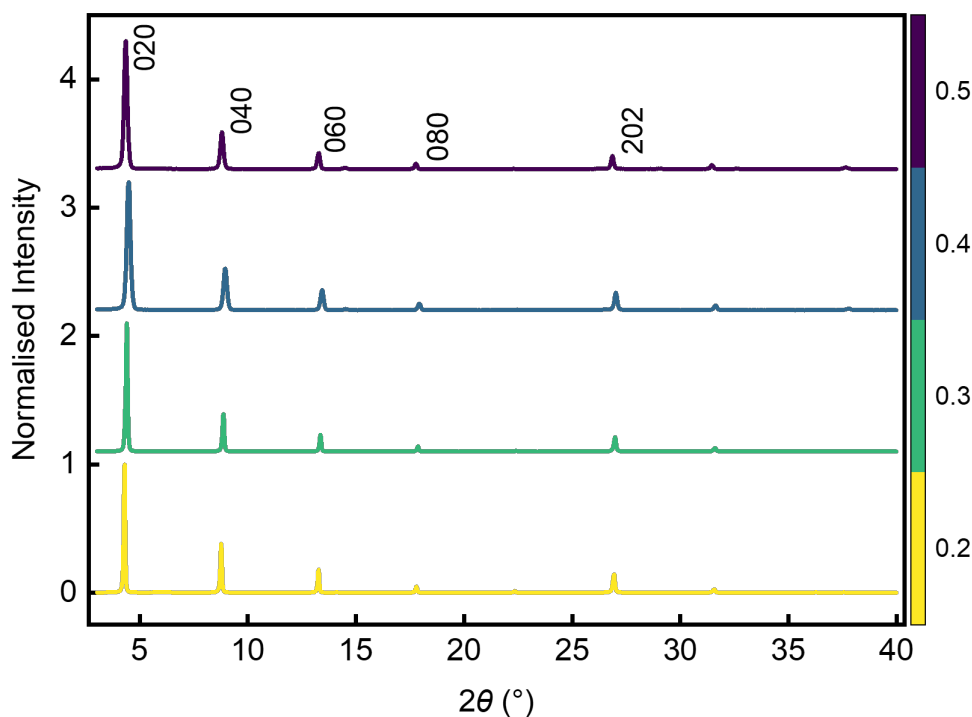


Figure 5.2: Normalised XRD patterns of a series of $\text{BA}_2\text{FAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$ films prepared from DMF/NMP with increasing Br incorporation. From bottom (yellow, $\text{BA}_2\text{FAPb}_2(\text{I}_{0.8}\text{Br}_{0.2})_7$) to top (purple, $\text{BA}_2\text{FAPb}_2(\text{I}_{0.5}\text{Br}_{0.5})_7$) in increments of 10% Br. The peaks are indexed following the convention of Stoumpos *et al.*³², with (0 2 k 0) R–P reflections indicated and an in-plane (202) reflection at higher angles.

to convert them into 3D perovskites using the same conversion process described in the previous chapter. However, during the conversion process, the films began to delaminate from the underlying substrate, resulting in very poor surface coverage.

To mitigate this issue, a 20 nm layer of aluminium oxide was deposited onto the FTO prior to perovskite deposition. To investigate whether this resolved the delamination issue, cross-sectional SEM (c-SEM) images were acquired. An example is shown in Figure 5.3.

The image reveals that the perovskite makes contact with the substrate at only a few isolated points and appears to be nearly fully detached elsewhere. Given that the ultimate aim of this work is to incorporate these perovskites into photovoltaic devices, this interfacial detachment presents a significant limitation. The bottom interface would likely exhibit extremely poor charge extraction properties, as the presence of an air gap would act as an insulating barrier and inhibit efficient charge extraction.

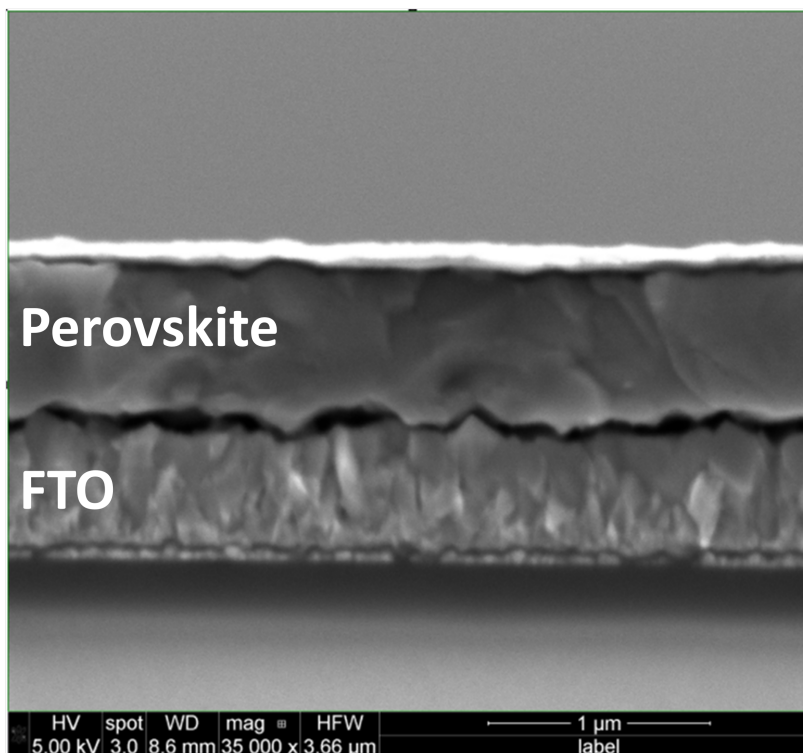


Figure 5.3: Cross-sectional scanning electron microscopy (C-SEM) image of $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ film prepared from DMF/NMP with an intermediate anneal. The image shows almost complete detachment between the substrate and the perovskite layer.

Although there was no immediately obvious explanation for this behaviour, it was consistently observed during the final high-temperature annealing step. One possible explanation is that the expulsion of significant amounts of BA during annealing generates voids at the bottom interface, leading to near-complete detachment. Similar macroscopic morphological issues have been reported in previous work using MeTHF/BA solvent systems, where they were mitigated by carefully controlling the BA content in the template.⁶⁵

Accordingly, the BA content in the template was reduced, deviating from the stoichiometric $n = 2$ Ruddlesden–Popper (R–P) composition. A new mixed 2D/3D template was prepared from a precursor solution comprising $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ and BA lead halide precursor in a 1:1 molar ratio, dissolved in DMF/NMP (see 3 for full details). The objective was to retain a fraction of crystalline 2D perovskite within the template, as this appeared to be important for stabilising the α -phase in the final 3D perovskite. The XRD diffractogram of these templates is shown below. From Figure 5.4, it is apparent that, for nearly all compositions (excluding 80% Br), prominent reflections corresponding to both 2D and 3D phases are present. The most prominent retained feature is the sub- 5° reflection, characteristic of the $(0, 2, 0)$ peak of the $n = 2$ Ruddlesden–Popper

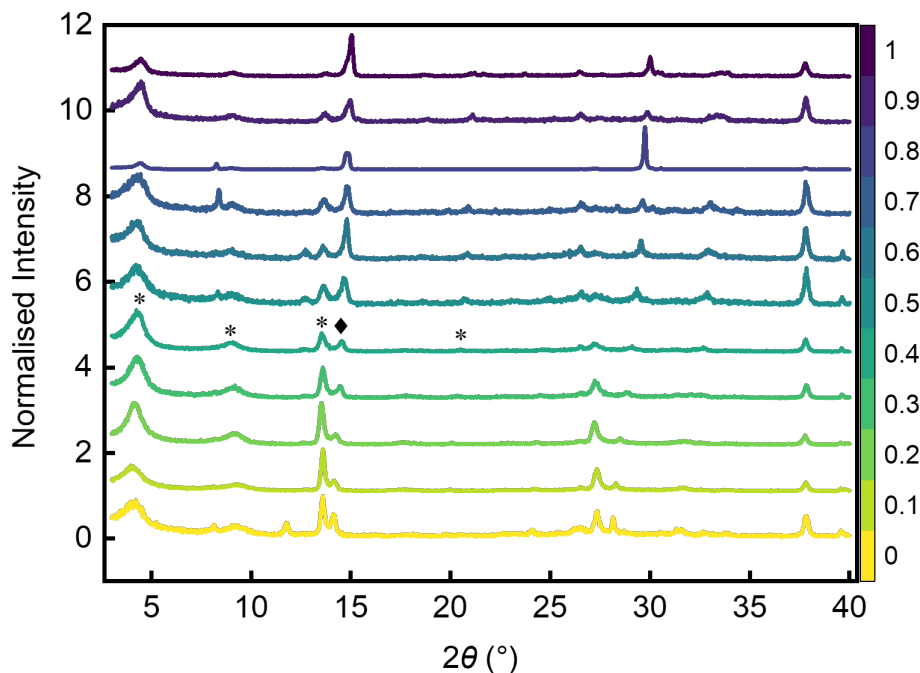


Figure 5.4: Normalised XRD patterns of mixed 2D/3D templates. The templates were made from a 1:1 molar ratio of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ and $\text{BAPb}(\text{I}_{1-x}\text{Br}_x)_3$, dissolved in DMF/NMP with intermediate anneals and increasing Br incorporation. From bottom (yellow, pure iodide) to top (purple, pure bromide) in 10% Br increments. The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase; asterisk – (0 2k 0) $n = 2$ R-P phase.

(R-P) phase. However, this reflection is broader and lower in intensity, indicating reduced crystallinity of the 2D phase within these films.

In addition, small contributions from the (100) reflection of the 3D perovskite phase are observed in the templates. This is particularly evident in the pure bromide composition, where a peak appears at approximately 15° . Given that the precursor solution was not stoichiometric with respect to a single phase, the presence of multiple phases is expected.

The conversion process was carried out identically to that used for the previous templates. Unlike the pure 2D templates, the C-SEM results shown in Figure 5.5 do not exhibit a dark air gap between the substrate and the perovskite film, suggesting that the modified template successfully alleviated the delamination issue. Furthermore, the SEM images reveal compact films with well-defined apparent grains, characteristic of standard FACs perovskites.⁶¹ Apparent grain sizes in such materials can range from tens of nanometres to micrometre scales, depending on factors

including additive chemistry, the underlying substrate, annealing conditions, and other processing parameters.⁴³ The grain sizes observed here fall within this typical range, which is encouraging. The uniform and compact morphology is also promising for photovoltaic applications, as it is generally associated with improved interfacial contact with charge transport layers and more efficient charge extraction. The SEM image of the film is shown in Figure 5.6.

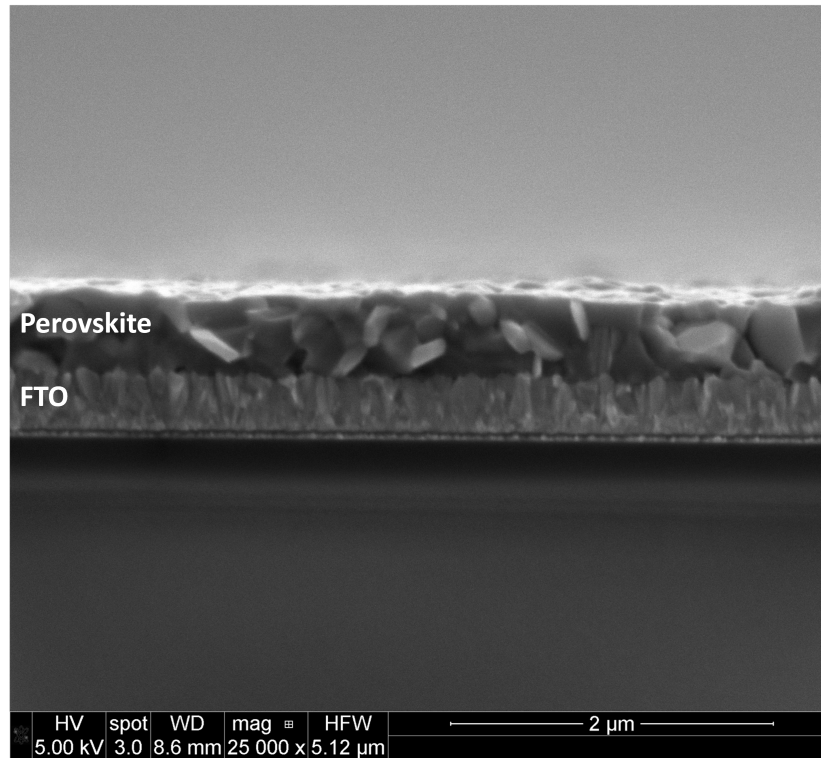


Figure 5.5: Cross-sectional scanning electron microscopy (C-SEM) image of $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ film prepared from a mixed 2D/3D template. The template was formed from $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ and $\text{BAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ in a 1:1 molar ratio dissolved in DMF/NMP with an intermediate anneal. The image shows uniform attachment between the substrate and the perovskite layer.

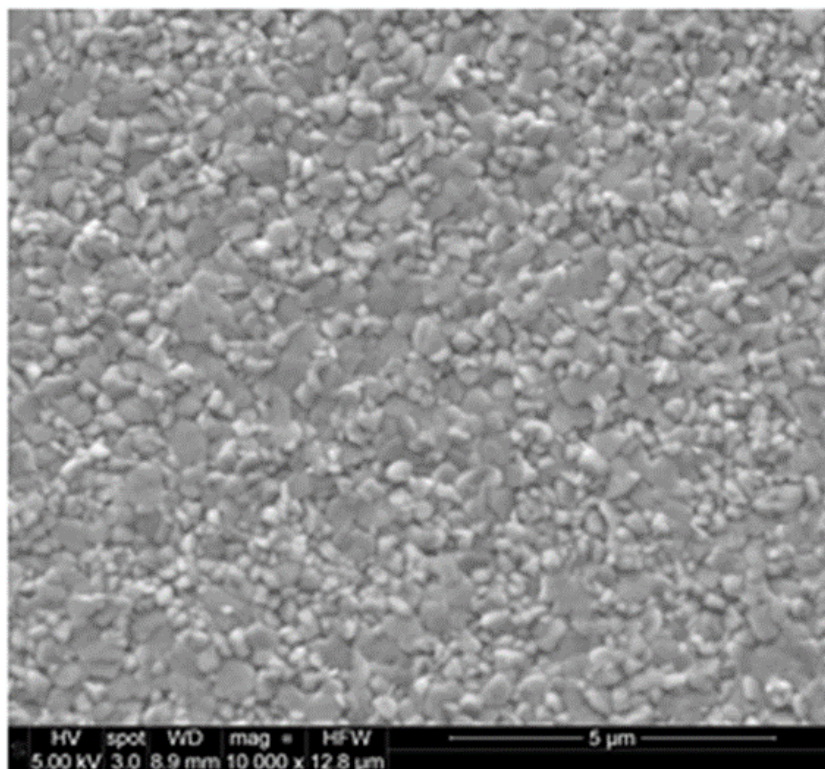


Figure 5.6: Scanning electron microscopy (SEM) image of $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ film prepared via 2D/3D templated processing.

Figure 5.7 shows images of the converted 3D films across the full compositional range. Unlike the one-step films shown in Figure 4.1, these films exhibit a consistent colour change from black to orange across the series. This visual progression is indicative of a gradual and systematic widening of the bandgap with increasing bromide content. The trend is consistent with that observed in FACs films reported by McMeekin *et al.*⁶¹.

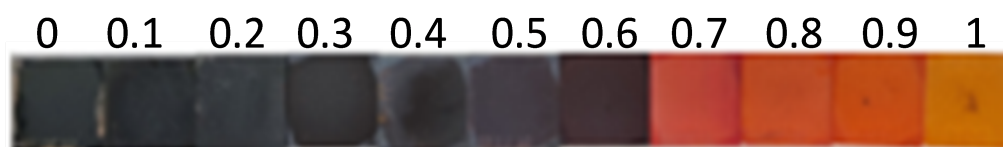


Figure 5.7: Photographs of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from mixed 2D/3D templates in DMF/NMP with increasing Br incorporation. From left to right: FAPbI_3 ($x = 0$) to FAPbBr_3 ($x = 1$) in 10% Br increments.

Despite these promising indications, as discussed in the previous chapter, it is the combination of UV–Vis and XRD data that demonstrates the successful stabilisation of the α -phase. These measurements were performed on 3D films prepared from the mixed templates, and the results are shown in Figures 5.10 and 5.8, respectively.

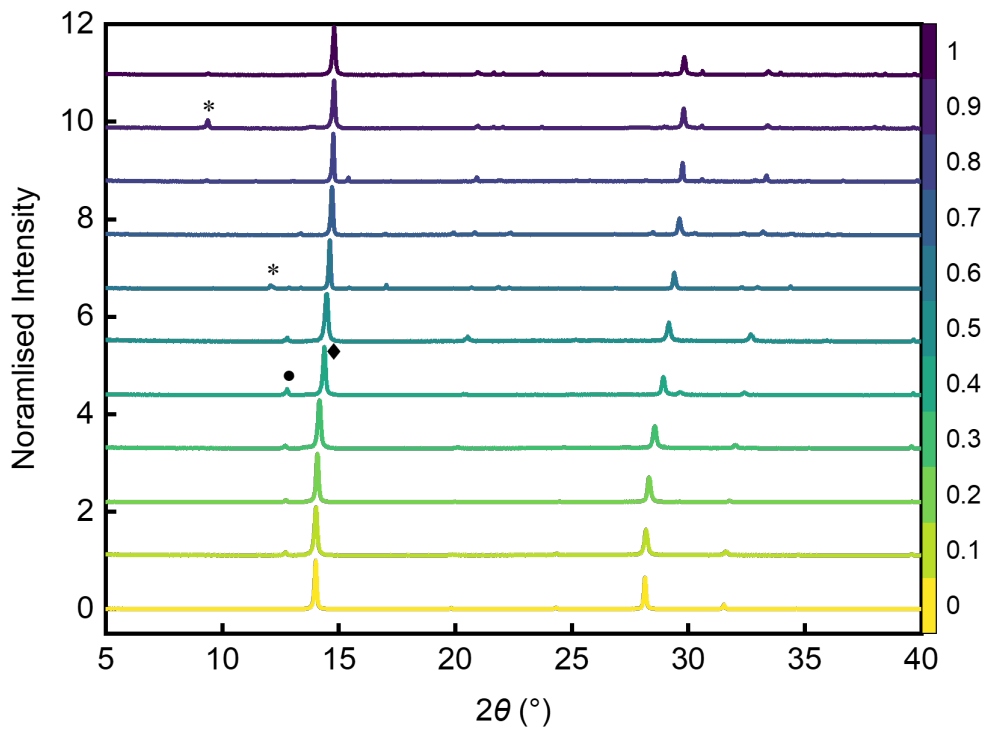


Figure 5.8: Normalised XRD patterns of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from mixed 2D/3D FA templates with increasing Br incorporation. From bottom (yellow, FAPbI_3) to top (purple, FAPbBr_3) in 10% Br increments. The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase, circle – (001) PbI_2 , and asterisk – (040) R-P phase.

The diffractograms show a consistent set of reflections across the entire compositional range, appearing at the expected diffraction angles. In Figure 5.9, a similarly consistent trend is observed in the (100) α -phase peaks, comparable to that seen in films prepared from MA templates in the previous section.

Concurrently, in Figure 5.10, the UV–Vis absorbance spectra show a clear and sharp onset at the expected bandgaps for each composition. It is worth noting a feature in the absorption of the 0% Br sample, which arises from the UV–Vis detector switching at 800 nm. The combination of XRD and UV–Vis measurements demonstrates that the mixed 2D/3D FA-templated processing route produces films with structural and optical properties consistent with $\alpha\text{-FAPb}(\text{I}_{1-x}\text{Br}_x)_3$.

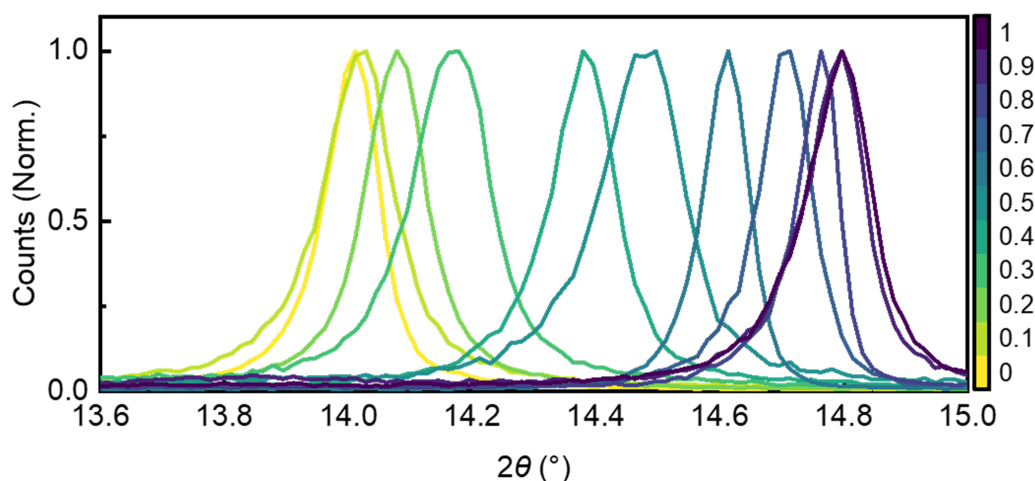


Figure 5.9: Normalised XRD patterns between 13.5° and 15° of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from mixed 2D/3D FA templates with increasing Br incorporation. From left (yellow, FAPbI_3) to right (purple, FAPbBr_3) in 10% Br increments.

However, despite the experimental evidence supporting this processing route, a theoretical explanation for why 2D templating circumvents the miscibility gap remains necessary. To gain further insight into the mechanism governing this crystallisation pathway, computational modelling was employed.

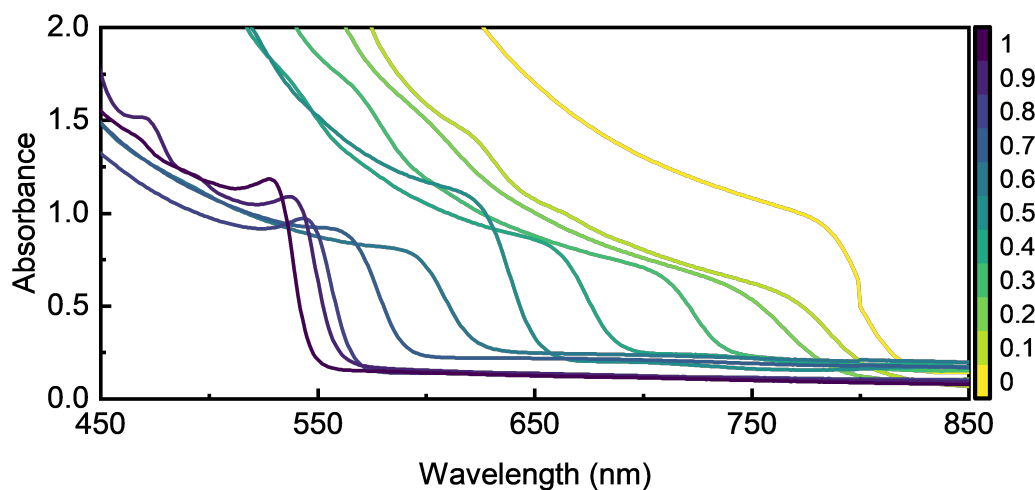


Figure 5.10: UV-Vis absorbance spectra of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films prepared from mixed 2D/3D FA templates with increasing Br incorporation. From right (yellow, FAPbI_3) to left (purple, FAPbBr_3) in 10% Br increments.

5.2.2 2D Modelling

The necessity of the 2D template suggests that there is an intrinsic structural or energetic feature that facilitates the formation of the α -phase perovskite in the final film. It was therefore appropriate to investigate the energetics of the $n = 2$ Ruddlesden–Popper (R–P) templates using the same MLIP-based approach applied to the 3D perovskite polymorphs (α - versus δ -phases) in the previous chapter.

The crystal structure of the 2D $\text{BA}_2\text{FAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$ template, specifically for the 30% bromide composition, is shown in Figure 5.11. In the figure, the blue arrows indicate axial halide sites, while the red arrows denote equatorial sites.

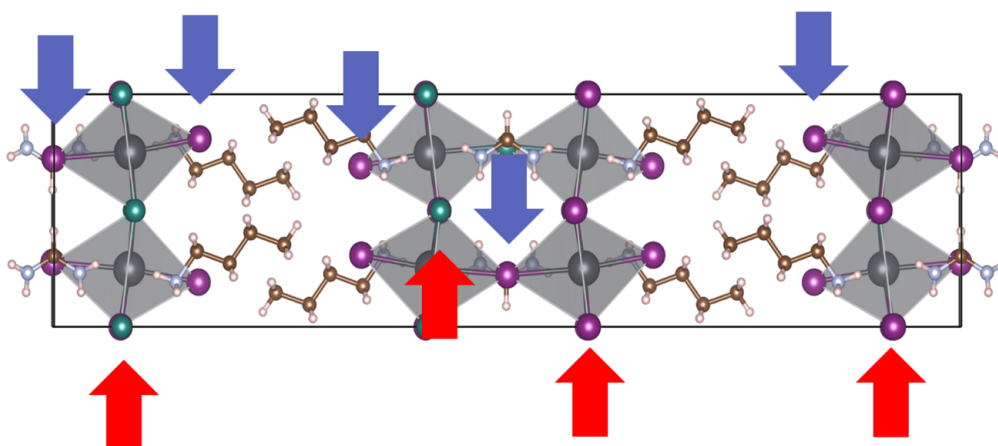


Figure 5.11: Schematic of $\text{BA}_2\text{FAPb}_2(\text{I}_{0.7}\text{Br}_{0.3})_7$ structure highlighting preferential site allocation for halide. Equatorial (red) and axial (blue) halide positions are shown. Purple spheres represent I^- , green spheres represent Br^- , large grey spheres represent Pb^{2+} , and the organic spacer layers correspond to BA^+ cations.

The modelling results provide insight into why the 2D template is effective in circumventing the miscibility gap. Figure 5.12 shows the enthalpy of mixing for $\text{BA}_2\text{FAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$ across the full compositional range. Across the entire composition space, the enthalpy of mixing remains close to zero, never exceeding 1.5 meV per halide. This indicates that halide mixing incurs a negligible enthalpic penalty and is therefore primarily driven by configurational entropy.

In contrast to 3D $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ compositions, this suggests that the 2D perovskite template does not exhibit a miscibility gap, consistent with the experimental observations presented earlier in the chapter. The key distinction lies in how the 2D structure accommodates local strain arising from the mixing of anions with different ionic radii (refer to Chapter 3 for full details of the model). The 2D structure contains crystallographically inequivalent halide sites, namely axial

and equatorial positions (highlighted in Figure 5.11). These inequivalent sites are absent in the cubic α -phase of the 3D perovskite, where all halide positions are symmetry-equivalent.

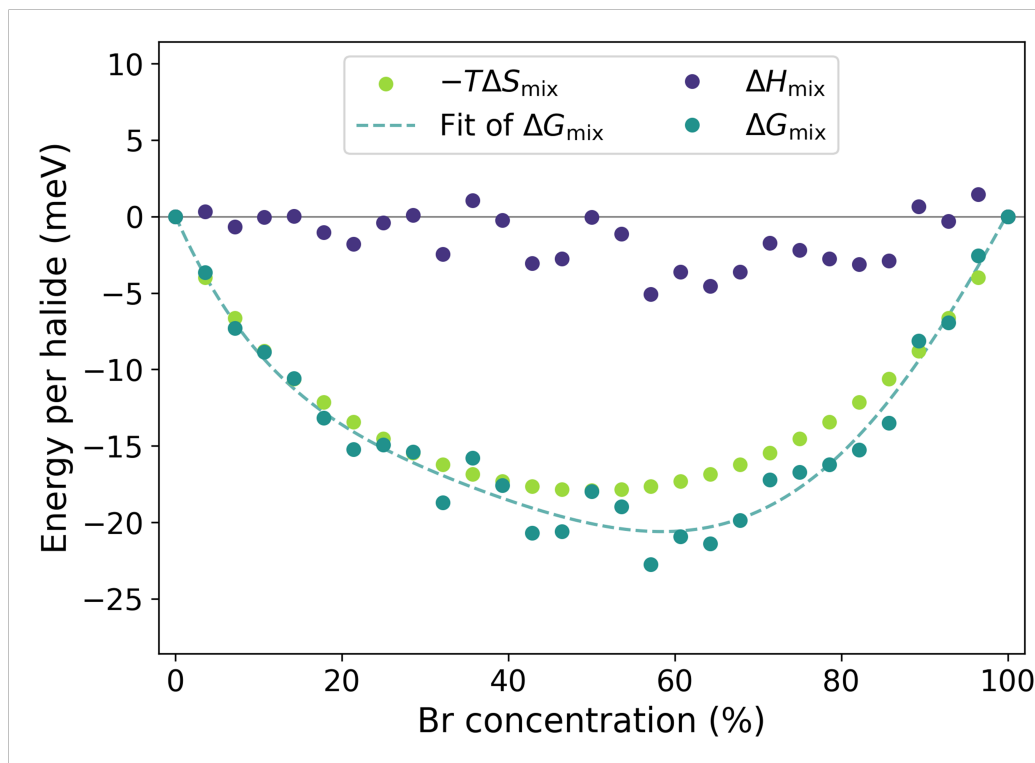


Figure 5.12: Computational modelling of $\text{BA}_2\text{FAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$ showing halide mixing thermodynamics, including enthalpic and entropic contributions at 300 K. The calculations were done by Tobias Loeff (Department of Materials, University of Oxford).

The mixing energetics reveal a consistent halide site preference: Br^- ions preferentially occupy equatorial positions, whereas I^- ions favour axial positions within the perovskite layers. This trend is illustrated in Figure 5.13, where the mixing energy is consistently lower across all compositions when a greater fraction of equatorial sites is occupied by Br^- . Such site-selective ordering reduces the mixing enthalpy and is consistent with previously reported trends.⁷⁸

The presence of crystallographically inequivalent halide sites in the 2D structure therefore enables the formation of stable corner-sharing octahedral networks with mixed halides across the full compositional range. In contrast, when crystallising the 3D perovskite directly from solution, the cubic α -phase lacks such inequivalent sites. Without the capacity to adopt energetically favourable halide configurations, lower-symmetry δ -phase motifs-containing face-sharing octahedra become energetically competitive. This competition between structural motifs gives rise to phase instability and ultimately manifests as the miscibility gap.

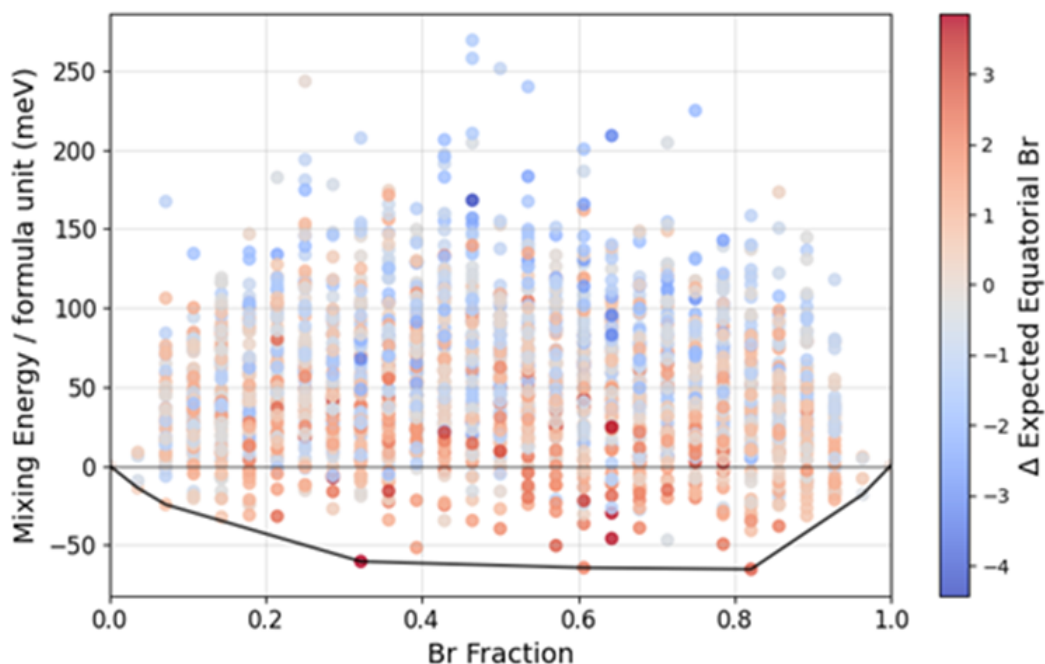


Figure 5.13: Computational modelling of $\text{BA}_2\text{FAPb}_2(\text{I}_{1-x}\text{Br}_x)_7$ showing halide mixing energetics as a function of bromide site occupancy. Blue and red markers correspond to bromide occupation at axial and equatorial sites, respectively. The expected number of equatorial Br atoms for a random distribution is $\langle N_{\text{Br}}^{\text{eq}} \rangle = \frac{16}{28} N_{\text{Br}}$. The colour scale represents the deviation from this value, $\Delta N_{\text{Br}}^{\text{eq}} = N_{\text{Br}}^{\text{eq}} - \frac{16}{28} N_{\text{Br}}$. The calculations were done by Tobias Loeff (Department of Materials, University of Oxford)

Therefore, the successful formation of the 3D mixed-halide α -phase appears to rely on two linked kinetic effects. First, the 2D template enables site-selective halide ordering, stabilising the desired mixed-halide distribution in corner-sharing octahedral networks. Second, as discussed in the previous chapter, the intermediate annealing step allows these mixed octahedra to be retained during cation exchange. The combination of these effects kinetically traps the α -phase structure. While the δ -phase remains thermodynamically competitive in the 20–55% Br region, the templated crystallisation pathway circumvents direct competition between the two polymorphs during film formation, yielding phase-pure 3D α -FAPb($\text{I}_{1-x}\text{Br}_x$)₃ that would otherwise be inaccessible through conventional solution processing.

5.2.3 BA as a bulk additive

However, given the complexity of this explanation, an alternative hypothesis is that the BA cation itself contributes to stabilisation of the mixed-halide perovskite phase. Indeed, it has been reported that the inclusion of 2D BA-based perovskite nanocrystals can kinetically stabilise FAPbI₃.⁶⁶ To investigate this possibility, proton nuclear magnetic resonance (¹H NMR) measurements were performed to quantify the BA content in the final films.

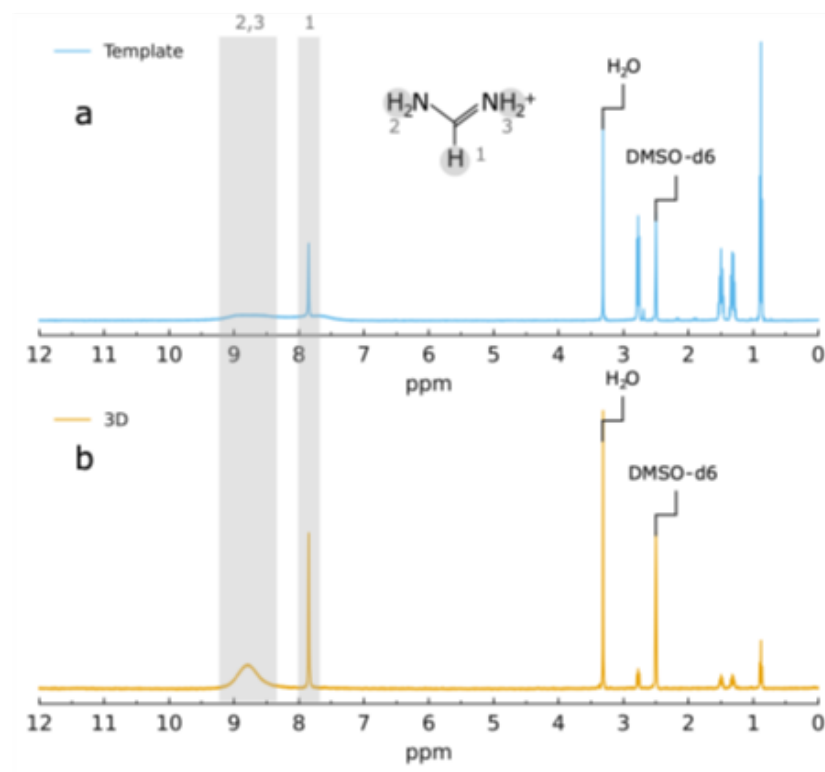


Figure 5.14: ¹H NMR spectra of template layer (a) and converted 3D film (b), dissolved in DMSO-d₆. Peaks correspond to the methine [CH (1)] and amine [NH₂ (2, 3)] protons of formamidinium. Measurements were done by Siyu Yan (Department of Physics, University of Oxford).

The NMR results indicate that the FA and BA contents are comparable in the templates. However, after conversion, the resulting films contain significantly more FA than BA, with BA present at most at ~10% relative to FA.

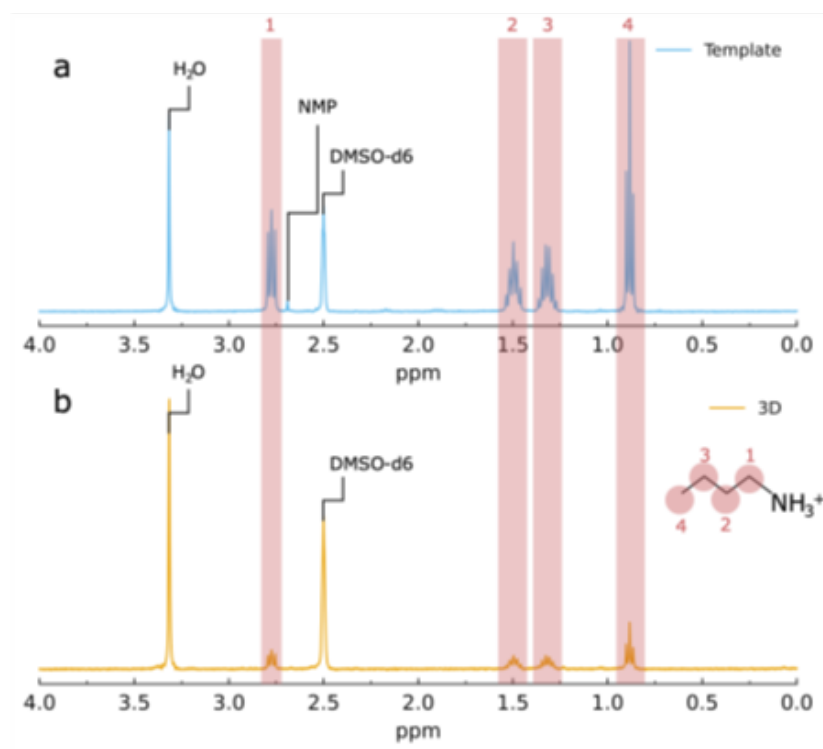


Figure 5.15: Low ppm region of the ^1H NMR spectra of template layer (a) and converted 3D film (b), dissolved in DMSO-d_6 . Signals corresponding to n-butylammonium are observed in both spectra. An additional peak at ~2.69 ppm in the template layer is attributed to residual NMP solvent. Measurements were done by Siyu Yan (Department of Physics, University of Oxford).

The presence of residual BA could therefore contribute to stabilising the α -phase. To test this possibility, control films were prepared by adding BA as a bulk additive to a $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ precursor solution in molar fractions of 0.5%, 1%, 5%, and 10%. The structural and optical properties of these films were characterised using XRD and UV-Vis spectroscopy. The XRD data is shown in Figure 5.16. No single well-defined reflection corresponding to the expected α -phase is observed in the diffractogram. Instead, the pattern suggests the presence of multiple phases, indicating that bulk incorporation of BA alone does not reproduce the phase-pure α -phase stabilisation achieved via 2D templating. Figure 5.17 further shows that no clear absorption onset is observed at the expected wavelength (approximately 750 nm) for the α -phase in the UV-Vis spectra. Instead, the absorption profile is inconsistent with that of phase-pure α - $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$. Taken together, these structural and optical measurements indicate that the simple addition of BA as a bulk additive is insufficient to circumvent the miscibility gap. Rather, successful stabilisation of the mixed-halide α -phase requires crystallisation to proceed through a 2D templating pathway.

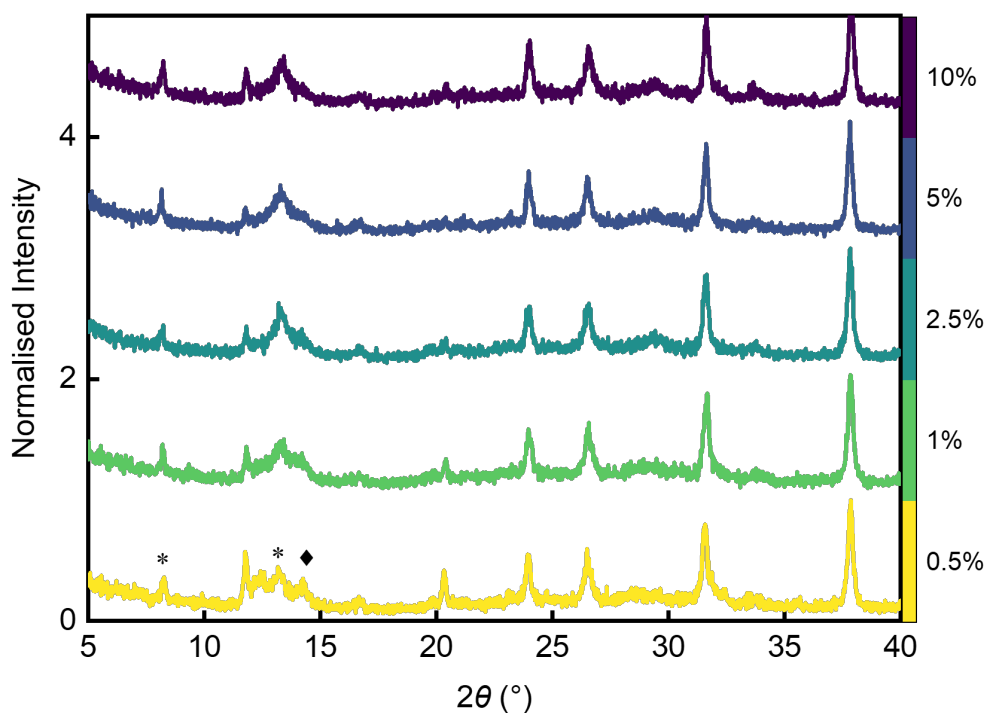


Figure 5.16: Normalised XRD patterns of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films made from 1-step DMF/DMSO with increasing amounts of BA in the precursor ink. From bottom (yellow pattern, 0.5% molar BA) to top (purple pattern, 10% molar BA). The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase, and asterisk – (02k0) R-P phase.

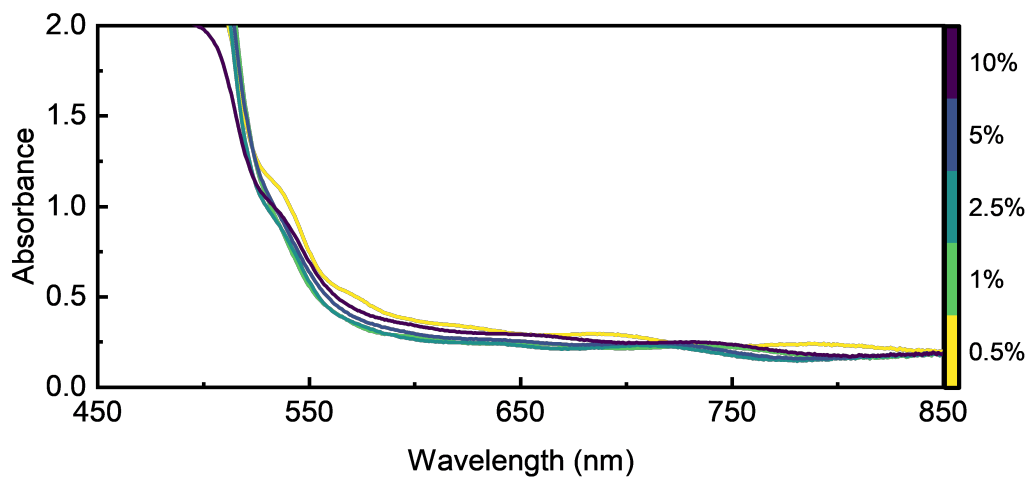


Figure 5.17: UV-Vis absorption spectra of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films made from 1-step DMF/DMSO with increasing amounts of BA in the precursor ink. From yellow trace (0.5% molar BA) to purple trace (10% molar BA).

5.2.4 Detailed characterisation of optoelectronic properties

Having established that this processing method successfully circumvents the miscibility gap and provided an explanation for its effectiveness, a more comprehensive characterisation of the films was undertaken. The 30% Br composition was selected for detailed analysis, as it lies at the centre of the miscibility gap and is therefore among the most challenging compositions to crystallise. Moreover, it has a bandgap which is close to optimum for incorporation into silicon perovskite tandems.²³ The bandgap of the perovskite was determined by applying an Elliott fit to the UV–Vis absorbance spectrum (see Figure 5.10). The film was found to have an optical bandgap of 1.75 eV.

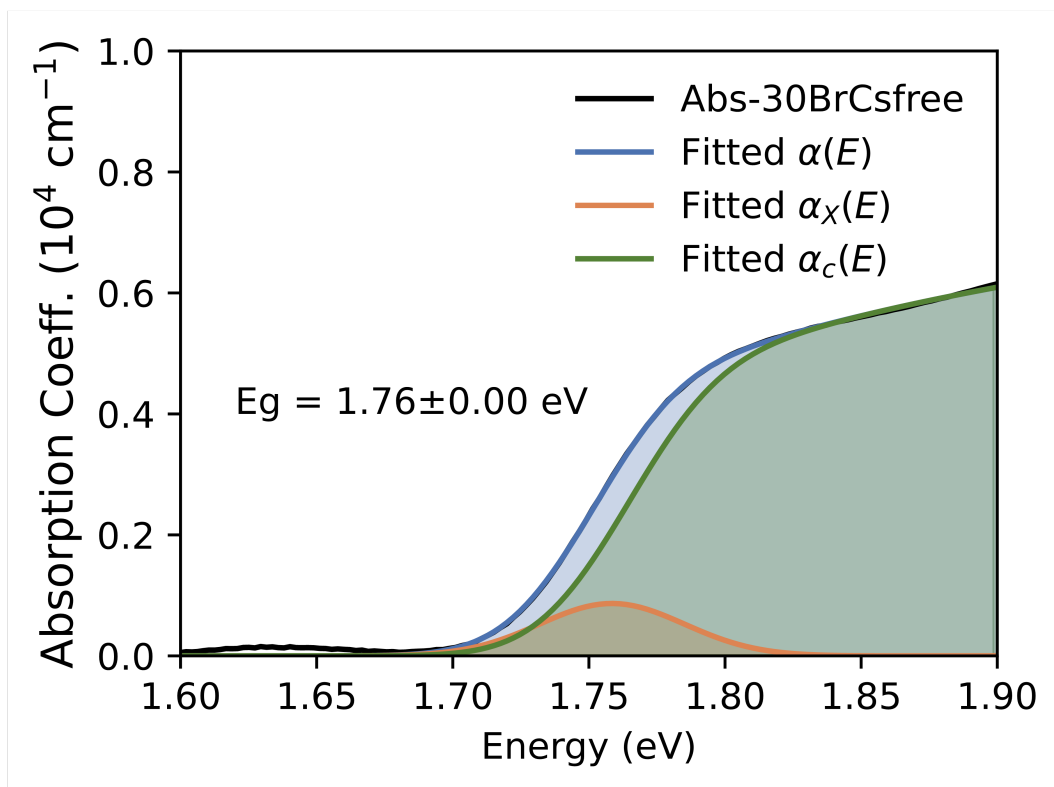


Figure 5.18: Elliott fitting of UV–Vis absorbance data for $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ made via 2D/3D templated processing. The calculated bandgap is 1.75 eV. The calculation was done by Siyu Yan (Department of Physics, University of Oxford).

To probe the carrier recombination pathways, photoluminescence quantum yield (PLQY) measurements were performed. The sample exhibited a PLQY of 1%. It is important to note that absolute PLQY values can vary significantly depending on the measurement setup; consequently, relative comparisons between samples measured using the same apparatus are often more meaningful. Nevertheless, the measured value lies within the typical range reported for perovskites with similar bandgaps.⁷⁹ The PLQY spectrum is shown in Figure 5.19.

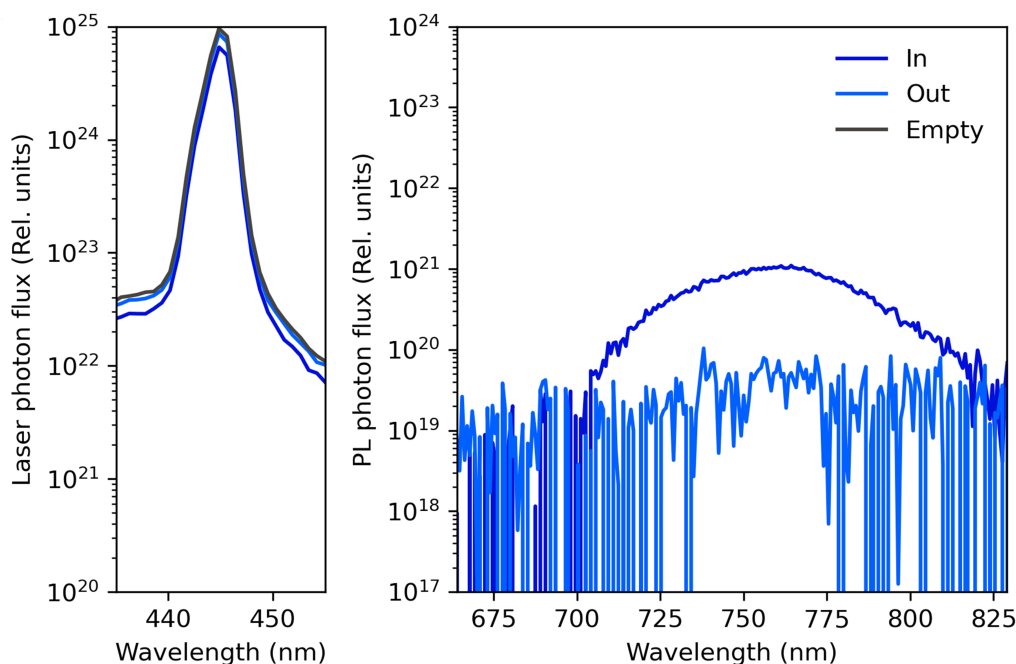


Figure 5.19: Photoluminescence quantum yield measurement. PLQY value of 1% for templated $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ measured on glass. The sample was excited with a 532 nm laser at an intensity normalised to 1 sun.

To investigate the charge carrier dynamics in more detail, spectrally resolved, fluence-dependent photoluminescence measurements were conducted. Figures 5.20a and 5.20b show spectrally and time-resolved photoluminescence (PL) data collected at increasing excitation fluence from 1.3 to $4.7 \mu\text{J cm}^{-2}$. While the PL intensity increases with fluence, there is no measurable spectral shift and the emission remains centred at $\sim 1.66 \text{ eV}$, indicating an absence of large spectral shifts due to reabsorption processes, bandgap renormalisation, or band-filling effects.^{80,81}

Figure 5.20b shows a normalised plot of fluence-dependent PL kinetics. Faster recombination is observed with increased excitation fluence, consistent with the growing contribution of higher-order recombination processes (i.e., bimolecular recombination, k_2).^{81,82} Figure 5.20c shows the fluence-dependent optical pump–terahertz probe (OPTP) kinetics, measured with a 3.1 eV pulsed laser excitation at fluences ranging between 2.1 and $5.9 \mu\text{J cm}^{-2}$. A linear fit of the initial $\Delta T/T$ amplitude against the charge-carrier density (Figure 5.20c inset) allows an in-film-plane, short-range, effective sum charge-carrier mobility, $\mu = 33 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, to be extracted. This mobility value is over an order of magnitude larger than that previously extracted for $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ (also utilising OPTP spectroscopy) and comparable to that of mixed FA–Cs systems, highlighting the exceptional crystalline quality of the thin film fabricated in our study.^{81,83}

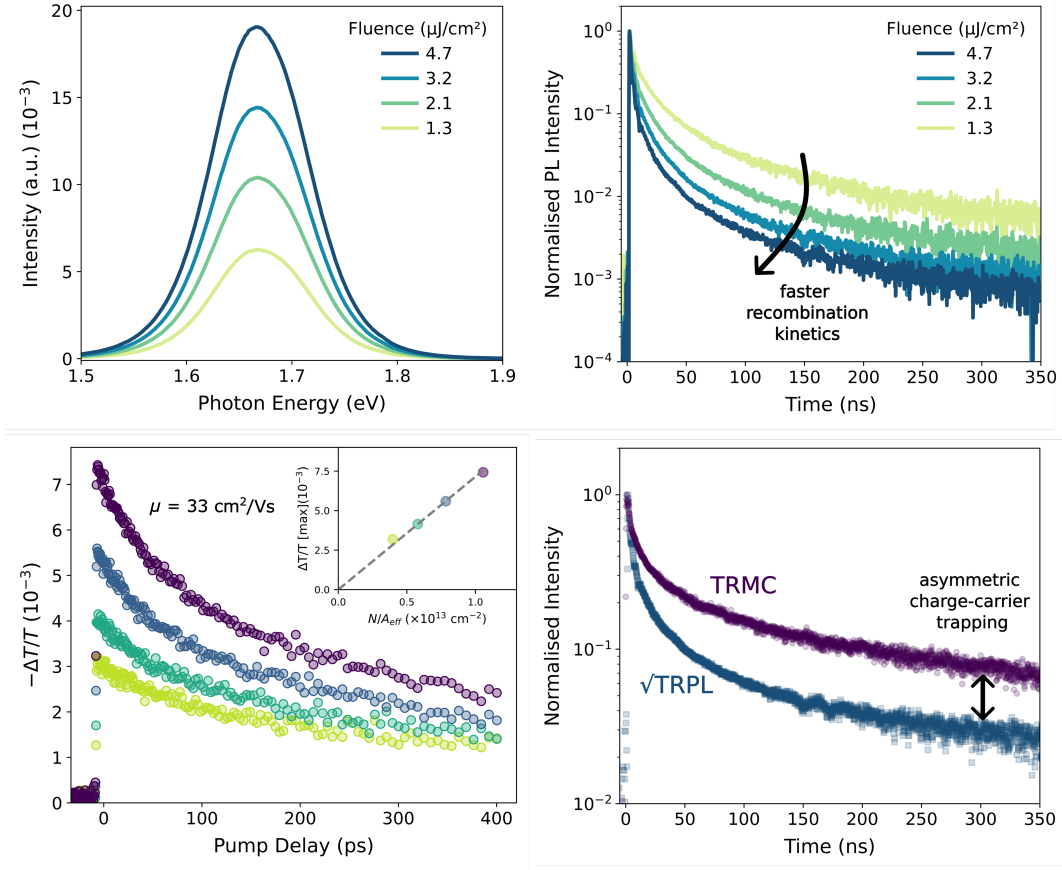


Figure 5.20: Fluence-dependent optical and photoconductivity characterisation using a 3.1 eV fs pulsed laser excitation. (a) Photoluminescence (PL) spectra collected under increasing excitation fluence. Emission intensities scale monotonically with fluence with minimal spectral reshaping. (b) Normalised time-resolved photoluminescence (TRPL) decays; higher fluences produce progressively faster decay components. (c) Optical-pump terahertz-probe (OPTP) photoconductivity transients measured as a function of excitation fluence (5.9 to $2.2 \mu\text{J cm}^{-2}$ from purple to green). The inset shows the fluence-dependent peak photoconductivity ($-\Delta T/T$ at $t = 0$) as a function of the injected carrier density; carrier mobility is extracted from a linear fit constrained through the origin. (d) Comparison between time-resolved microwave conductivity (TRMC) and TRPL measurements, taken *in situ* at the same fluence ($4.7 \mu\text{J cm}^{-2}$). TRMC and square-rooted TRPL dynamics show a clear divergence, highlighting asymmetric electron and hole trapping kinetics. Measurements were taken by Bembe Cameron Macintosh (Department of Physics, University of Oxford).

Normalised *in situ* time-resolved microwave conductivity (TRMC) and square-rooted time-resolved photoluminescence (TRPL) transients are shown in Figure 5.20d and are compared at the same fluence. The TRMC and square-rooted TRPL signals exhibit differing dynamics, with the TRMC signal decaying more slowly. Such kinetics can be attributed to asymmetric trapping of charge carriers: one carrier species is preferentially trapped in a retaining trap state, preventing recombination of the opposite carrier and leading to a remanent photoconductivity signal.^{84,85}

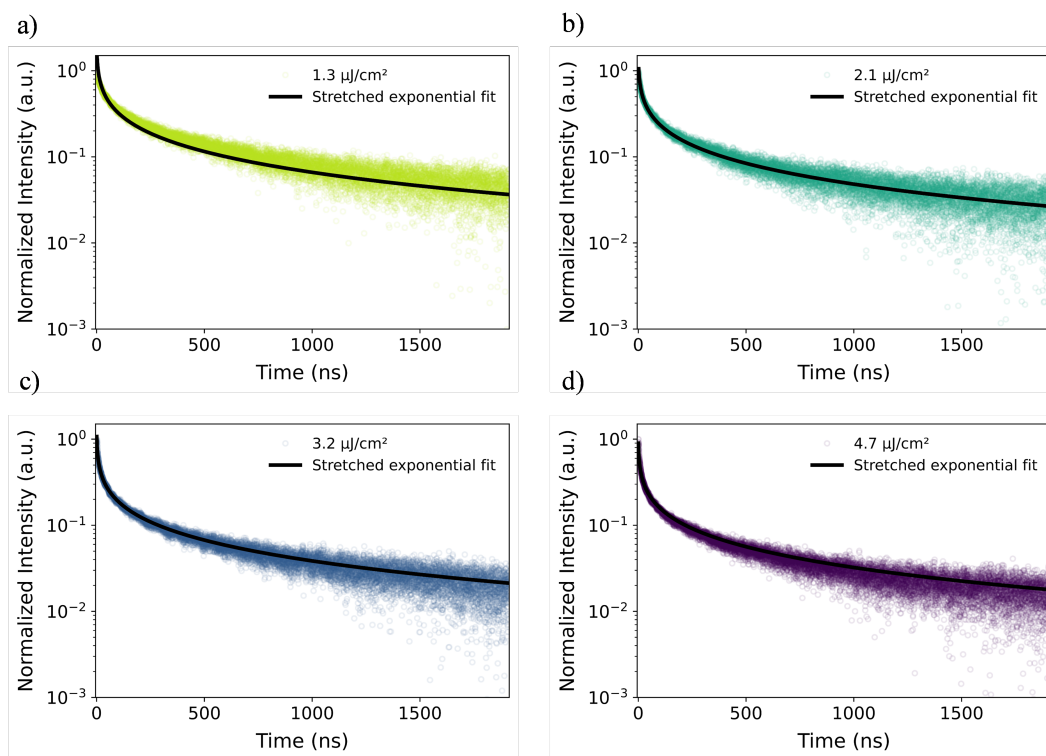


Figure 5.21: Time-resolved microwave conductivity (TRMC) measurements measured at different excitation fluences. Solid lines represent a globally fitted stretched exponential decay function, yielding τ and β parameters. Measurements were taken by Bembe Cameron Macintosh (Department of Physics, University of Oxford).

The average lifetime of the charge carriers was calculated by applying a global fit to the fluence-dependent TRMC data, shown in Figure 5.21, using a stretched exponential of the form $I = A \exp \left[-(t/\tau)^\beta \right]$. The average carrier lifetime was determined as $\langle \tau \rangle = 76.6$ ns, which, together with the extracted mobility value, yielded a diffusion length of $L_D = 2.5 \mu\text{m}$.^{86,87}

Taken together, these measurements demonstrate that the 2D/3D-templated perovskites possess properties that are highly promising for photovoltaic applications. The combination of long carrier lifetimes, high mobilities, and favourable film morphology makes them well-suited for incorporation into solar cell devices.

5.2.5 Devices

To test the viability of the templated perovskites in photovoltaic devices, they were incorporated into p-i-n devices. The architecture of the devices is shown in Figure 5.22. The performance of the champion device is shown in Figure 5.23. The cell exhibits a stabilised power conversion efficiency (PCE) of 17.1%, with an open-circuit voltage (V_{oc}) of 1.22 V, a short-circuit current density (J_{sc}) of 18.6 mA cm^{-2} , and a fill factor (FF) of 0.72. The batch statistics are shown in Figure 5.24

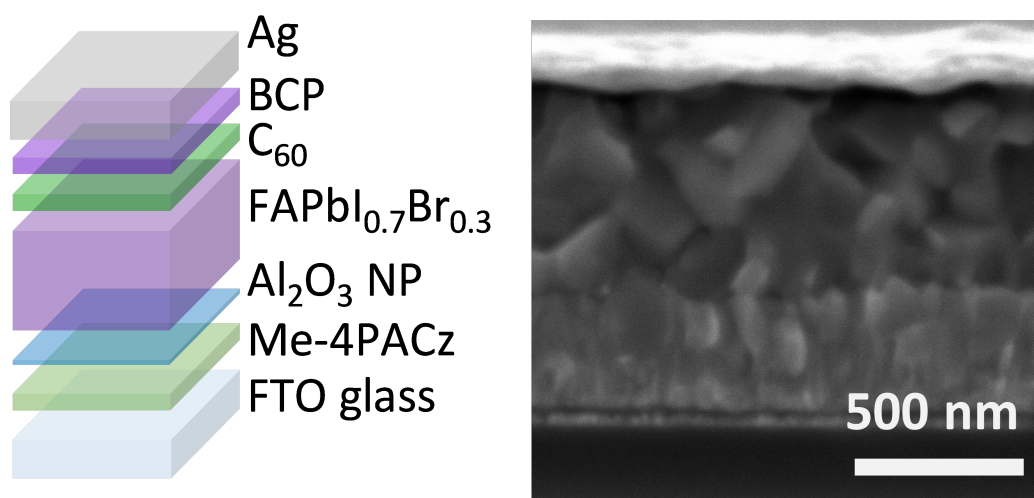


Figure 5.22: Schematic and cross-sectional SEM image of the device shown side by side. The stack was as follows (bottom to top): FTO, alumina nanoparticles, perovskite, C_{60} , BCP, and silver.

To further assess the quality of photogeneration and charge collection, external quantum efficiency (EQE) measurements were performed. The integrated J_{sc} calculated from the EQE spectrum is 18.7 mA cm^{-2} , in excellent agreement with the value obtained from the $J-V$ measurements. An operational bandgap of 1.68 eV was extracted from the EQE data, which is consistent with previously reported values for similar $FACsPb(I_{0.7}Br_{0.3})_3$ compositions, accounting for the slight bandgap widening typically induced by Cs incorporation.⁶¹

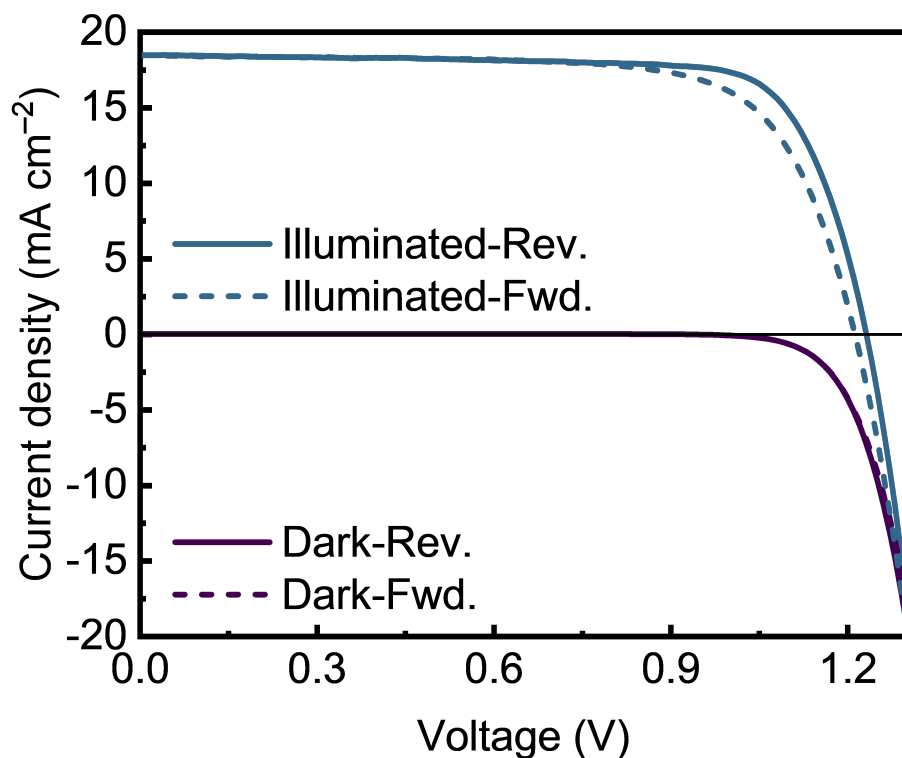


Figure 5.23: Device J - V characteristics. Current-voltage (J - V) curve of the champion device, measured at a scan rate of 0.1 V s^{-1} .

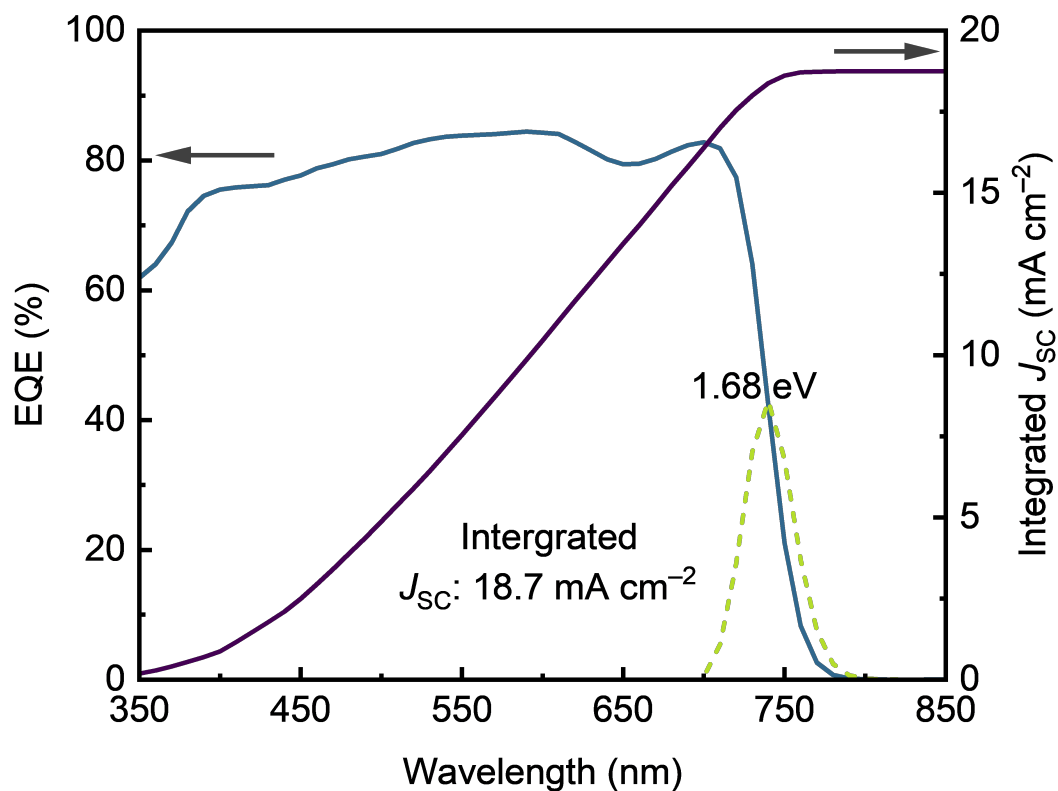


Figure 5.25: EQE spectrum measured in short-circuit (J_{sc}) configuration for the highest-efficiency perovskite cell, with integrated J_{sc} and derived bandgap plotted. The bandgap was calculated by determining the wavelength at which $d(\text{EQE})/d\lambda = 0$.

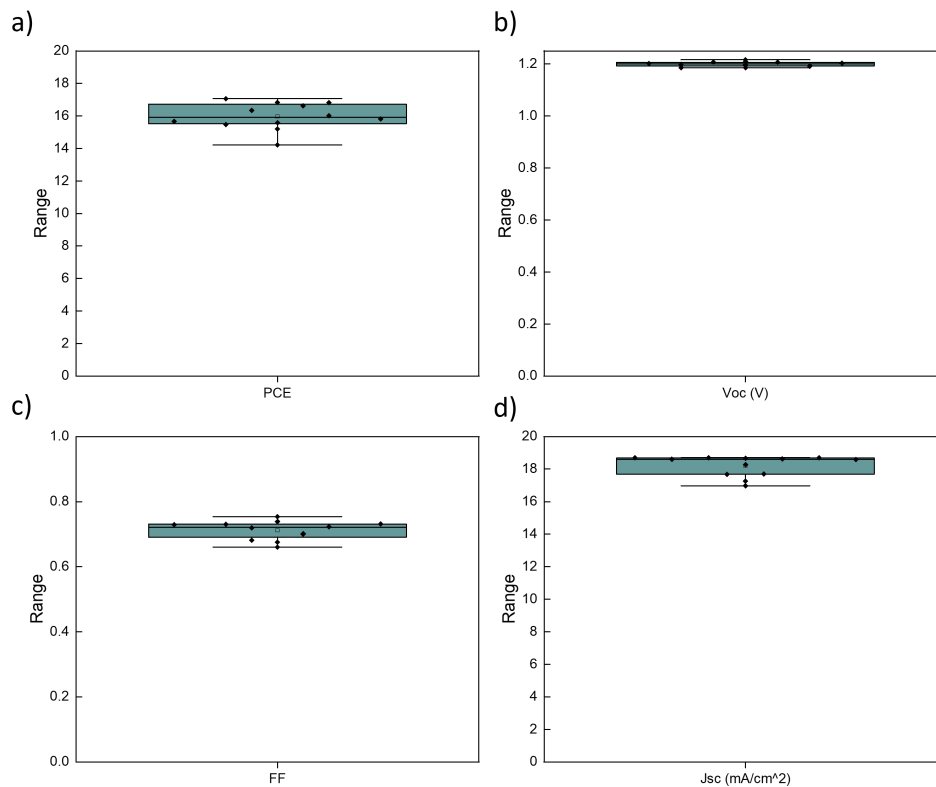


Figure 5.24: Batch statistics for FAPb(I_{0.7}Br_{0.3})₃ devices. (a) PCE, (b) V_{oc} , (c) FF, (d) J_{sc} .

Optimised FACs perovskites with comparable bandgaps can achieve J_{sc} values approaching 21 mA cm^{-2} and PCEs as high as 23%.⁸⁸ While the performance metrics reported here do not yet reach state-of-the-art levels, it is important to note that FA-pure perovskites have not previously been successfully fabricated at this bandgap, and the present devices were not subject to extensive optimisation. Within this context, a stabilised PCE of 17.1% represents a strong proof-of-concept for the viability of the templated mixed-halide films in photovoltaic devices.

One possible limitation to the device performance may arise from the asymmetric charge trapping inferred from the TRPL and TRMC measurements discussed above. Such trapping could contribute to non-radiative recombination losses and limit both the fill factor and open-circuit voltage. These observations suggest that further improvements in performance may be achievable through refinement of the crystallisation process to reduce trap densities, as well as through optimisation of the device stack and interfacial layers.

5.2 CONCLUSION

In this chapter, the miscibility gap in mixed-halide $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskites has been successfully circumvented through a 2D/3D templated processing route. Using MLIP-based modelling, a mechanistic explanation has been proposed to rationalise why 2D templates facilitate stabilisation of the 3D α -phase. Specifically, the presence of crystallographically inequivalent halide sites in the 2D structure enables favourable halide ordering and suppresses the enthalpic driving force for phase separation. These insights provide a new conceptual framework for understanding and controlling phase stability in mixed-halide perovskites.

The optoelectronic properties of the templated perovskites have been comprehensively characterised, revealing long carrier lifetimes, high mobilities, and favourable film morphology. While certain limitations (such as asymmetric charge trapping) remain, the overall material quality compares well with established FACs systems of similar bandgap. Incorporation into p-i-n photovoltaic devices further demonstrates the viability of these materials as semiconductors for solar cell applications. Although the device efficiencies do not yet reach state-of-the-art values, the results represent a strong proof of concept, and there remains significant scope for optimisation of both film processing and device architecture.

The following chapter extends this work by reintroducing Cs into the templated perovskite system. This will address a central question in the field: does the inclusion of Cs intrinsically enhance performance and stability, or has its apparent benefit primarily arisen from the absence of alternative stabilisation strategies? By combining templated processing with controlled compositional variation, the next chapter aims to disentangle these effects and provide further insight into the role of Cs in mixed-halide perovskites.

IMPACT OF C_s AND TEMPLATING ON STABILITY

6.1 INTRODUCTION

The preceding two chapters addressed the problem of the miscibility gap in FA-based mixed-halide perovskites. They explored both the origin of the miscibility gap and the development of an alternative crystallisation pathway to circumvent it, enabling the formation of α -FAPb(I, Br)₃ across the full range of halide compositions. Although the devices fabricated at the end of Chapter 5 demonstrated the viability of this new material as a photovoltaic absorber, they showed considerable scope for optimisation. However, device optimisation is not the focus of this chapter. Instead, this chapter aims to address more fundamental questions regarding the stability of the α -phase in perovskites.

As discussed in the introduction to Chapter 4, mixed-halide perovskites are typically processed using a mixture of FA and Cs at the A-site in order to overcome the miscibility gap.⁶¹ In Chapter 4, it was proposed that the miscibility gap originates from a degeneracy in the formation energy of competing phases in FAPb(I, Br)₃, driven by macroscopic lattice strain arising from the large size of the FA cation. This explanation can be extended to rationalise why introducing Cs into the perovskite circumvents the gap. Partial substitution of FA with the smaller Cs cation reduces the average A-site ionic radius, thereby lowering macroscopic lattice strain and enabling the formation of the corner-sharing lead–halide octahedral network around the A-site.

Whilst FACs compositions demonstrate impressive efficiencies, researchers have highlighted the propensity of mixed A-site α -phase compositions to segregate irreversibly into non-photoactive phases comprising FA-rich and Cs-rich domains. It has also been reported that this tendency for demixing is directly related to the initial homogeneity of A-site cation distribution: the more uniformly mixed the perovskite, the more resistant it is to phase segregation.^{41,42}

Relating stability to compositional homogeneity highlights the potential for the templated processing developed in Chapter 5 to influence material stability. As previously discussed, templated processing circumvents the miscibility gap by promoting more homogeneous halide incorporation

into preferential lattice sites present in the 2D phase. If this enhanced homogeneity can be extended to mixed A-site compositions, it may lead to improved stability. To test this hypothesis, the stability of films with identical compositions (in terms of Cs and halide content), but processed via conventional one-step and 2D-templated routes, will be compared. This constitutes one of the primary aims of this chapter.

The second aim is to better understand the role of Cs in determining perovskite stability. The influence of Cs incorporation in FA-based perovskites has been widely studied.^{42,89–91} In addition to stabilising the photoactive α -phase, partial substitution of FA with Cs has been shown to improve structural and environmental stability in mixed-cation perovskites.⁶¹ Furthermore, Cs incorporation has been reported to modify several material properties, including crystallinity, defect density, and film morphology, which in turn influence charge-carrier dynamics and device performance.^{42,90–92}

A number of studies investigating compositions with Cs contents in the range of a few percent up to $\sim 30\%$ have shown that increasing Cs concentration can improve film quality and stability up to an optimal threshold.^{61,90,91} However, higher Cs contents have been associated with increased compositional heterogeneity, less uniform film morphology, and enhanced susceptibility to photoinduced phase segregation, effects that are often attributed to differences in the crystallisation kinetics of FA- and Cs-containing perovskite phases.^{42,90,92} Consequently, optimised compositions reported in the literature typically contain $\sim 15\text{--}20\%$ Cs, balancing improved stability and optoelectronic properties against the onset of phase segregation and increased disorder.^{42,61,91}

It is important to note that many of these findings are based on studies of pure iodide perovskites, reflecting early interest in single-junction-relevant compositions and the reduced compositional complexity of such systems. In contrast, this chapter focuses on mixed-halide compositions, for which the influence of Cs remains less comprehensively understood. Moreover, previous studies have generally lacked a pure FA-based control sample for comparison. As this work has developed a method to produce phase-pure α -phase FA-based perovskites, it provides a unique opportunity to carry out a more rigorous and controlled investigation.

In this chapter, varying amounts of Cs will therefore be incorporated into $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films using 2D-templated processing. The material and optoelectronic properties of the films will then

be characterised. Once an optimal composition has been identified, the intended comparisons can be made. Specifically, this chapter aims to determine whether improved A-site homogeneity has a greater impact on stability (by comparing templated and one-step processed films of identical composition), or whether the complete elimination of Cs is more critical (by comparing templated films with and without Cs).

6.2 RESULTS AND DISCUSSION

6.2.1 The effect of incorporating Cs in films via templated processing

To incorporate Cs into the films, FA salts were partially substituted with Cs salts in the precursor ink for the 2D/3D template. The conversion solution consisted of the same FAI/FABr mixture for all compositions. Cs was introduced in 5% increments from 0% to 25%, with the exception of an additional 17.5% Cs composition, as this concentration is commonly cited in the literature as optimal for device performance and therefore provides a salient comparison.⁶¹

Before conversion, the templates were characterised to determine whether the introduction of increasing Cs content altered their properties. The UV–Vis absorption spectra of the templates are shown in Figure 6.1.

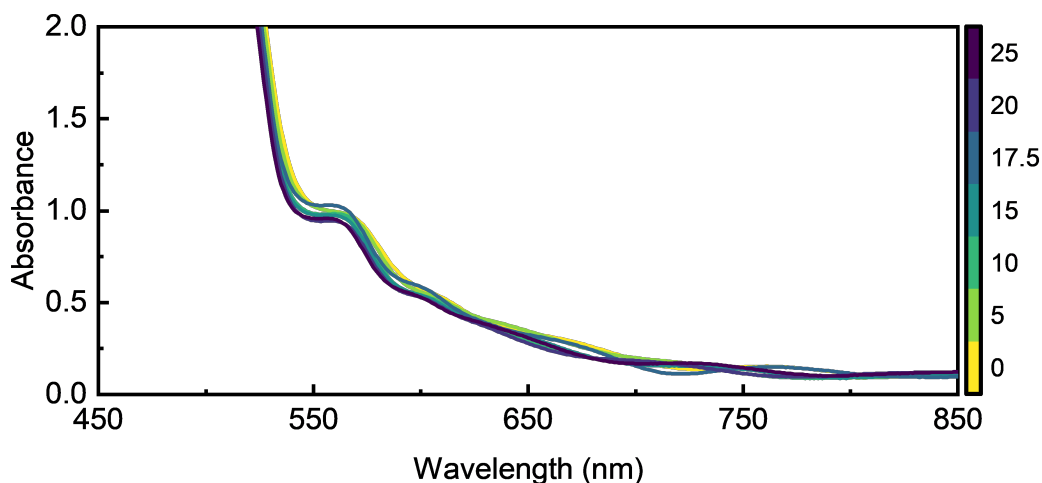


Figure 6.1: UV–Vis absorbance spectra of 2D/3D templates made by combining a 1:1 molar ratio of $\text{BAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ and $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films with increasing Cs incorporation. The spectra progress from right (yellow pattern, pure FA, $y = 0$) to left (purple pattern, 25% Cs, $y = 0.25$).

No significant changes are observed in the main features of the absorption spectra as the Cs content increases. However, the absorption onset associated with the 2D phase (between 550 and 600 nm) exhibits a slight blue shift with increasing Cs content. This shift indicates incorporation of Cs into the lattice, as a widening of the bandgap is expected when the average size of the A-site cation decreases.

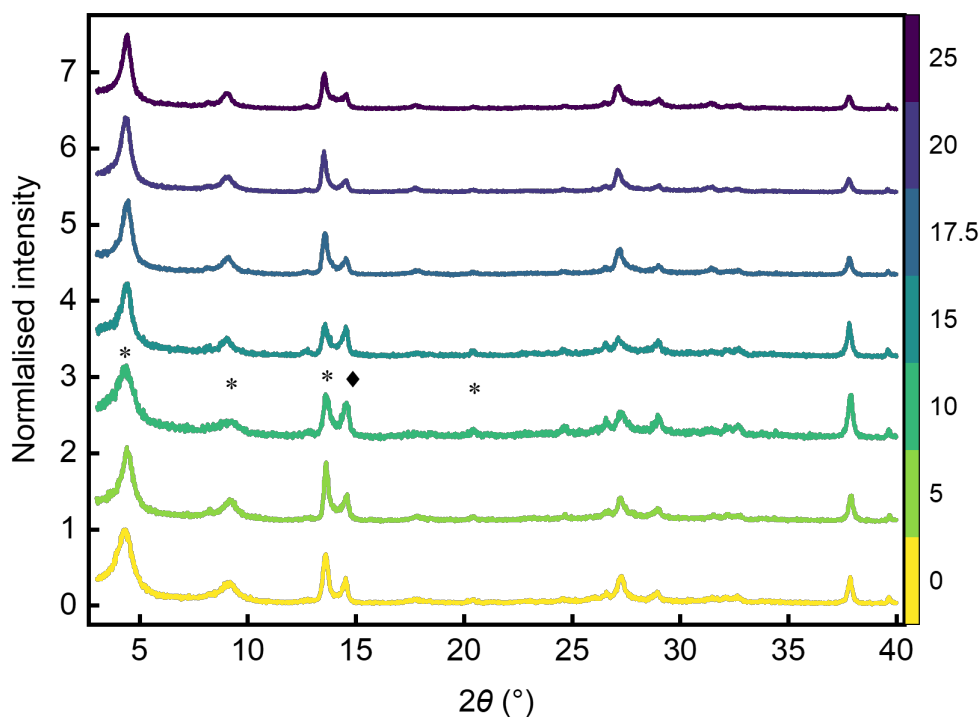


Figure 6.2: Normalised XRD patterns of 2D/3D templates made by combining a 1:1 molar ratio of $\text{BAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ and $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films with increasing Cs incorporation. The spectra progress from bottom (yellow pattern, pure FA, $y = 0$) to top (purple pattern, 25% Cs, $y = 0.25$). The key for the reflections marked by symbols is as follows: diamond – (100) α -perovskite phase; asterisk – (0 2 k 0) $n = 2$ R–P phase.

Additional structural changes (or the absence thereof) are captured in the XRD patterns of the templates shown in Figure 6.2. For all templates, the same 4.2° (020) reflection (and higher order (02 k 0) reflections) of the $n = 2$ Ruddlesden–Popper (R–P) phase is observed as well as the α -phase at 14.3° . As discussed in Chapter 5, the presence of a small fraction of the R–P phase in the templates is essential for the kinetic stabilisation of the α -phase in the converted films.

Having established evidence of Cs incorporation into the lattice, as well as the presence of the 2D phase in the templates, the next step was to convert the films in the same manner as described in Chapter 5. The UV–Vis absorption spectra of the converted films are shown in Figure 6.3. The absorption exhibits a sharp onset around 750 nm for all compositions ranging from 0% to 25% Cs. A slight but distinct blue shift is again observed with increasing Cs concentration.

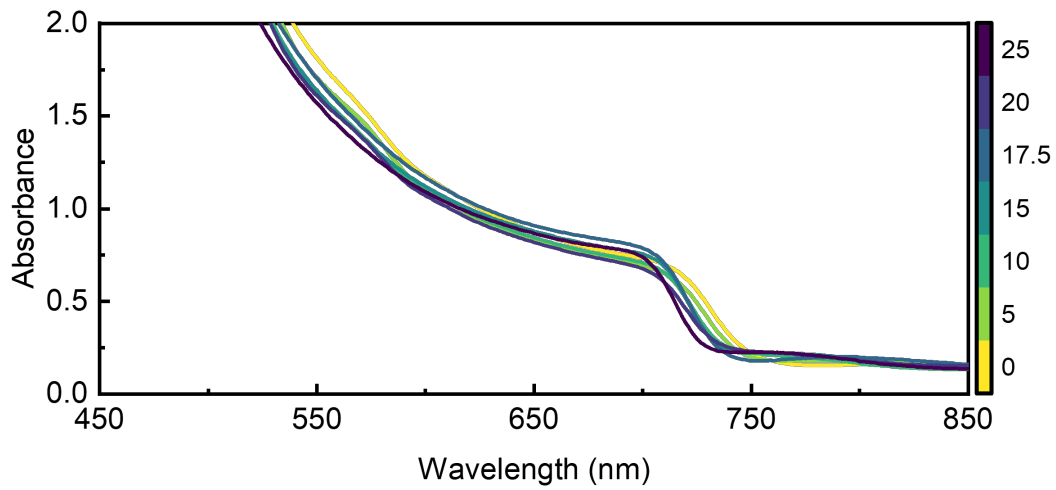


Figure 6.3: UV–Vis absorbance spectra of converted $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via 2D templated deposition with increasing Cs incorporation. The spectra progress from right (yellow pattern, pure FA, $y = 0$) to left (purple pattern, 25% Cs, $y = 0.25$).

Although the spacing between the absorption onsets is not perfectly uniform, the overall trend clearly shows a progressive blue shift. This further supports the conclusion that Cs is being incorporated into the lattice. The uneven spacing may arise from small deviations in precursor stoichiometry, as each composition was prepared and weighed separately.

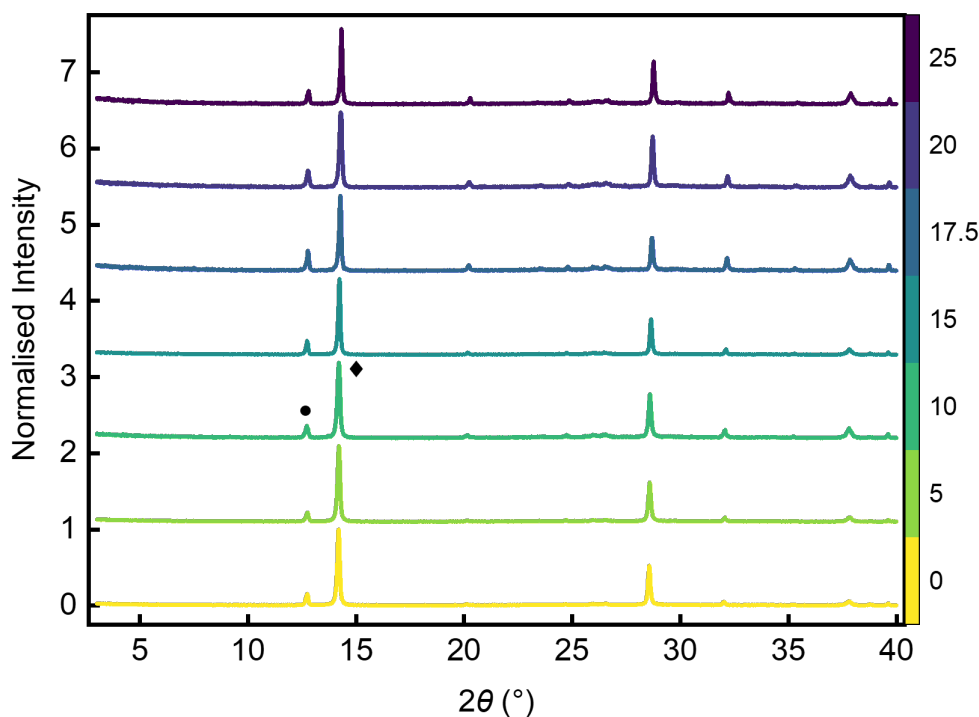


Figure 6.4: Normalised XRD patterns of converted $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via 2D templated deposition with increasing Cs incorporation. The spectra progress from bottom (yellow pattern, pure FA, $y = 0$) to top (purple pattern, 25% Cs, $y = 0.25$).

The XRD diffractogram in Figure 6.4 also suggests that both the conversion and Cs incorporation were successful, as clear reflections corresponding to the (100) α -phase are observed for each composition. Together, the UV-Vis and XRD results indicate that Cs is successfully incorporated into the final films in the form of $\alpha\text{-FACsPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$.

In Figure 6.5, the unnormalised XRD patterns are shown focusing on the region containing the (100) α -phase reflection. The shift of the reflections to higher angles with increasing Cs content further reinforces the claim that Cs is being incorporated into the lattice, as a reduction in the lattice parameter results in reflections appearing at higher 2θ values.³⁰

The figure also reveals the first notable divergence from trends commonly reported in the literature, namely that Cs incorporation is often reported to improve the crystallinity of perovskite films.⁹¹ In the case of 2D-templated deposition, however, the opposite trend is observed. A reduction in the intensity of the (100) reflection is evident, which suggests decreased crystallinity of the α -phase.

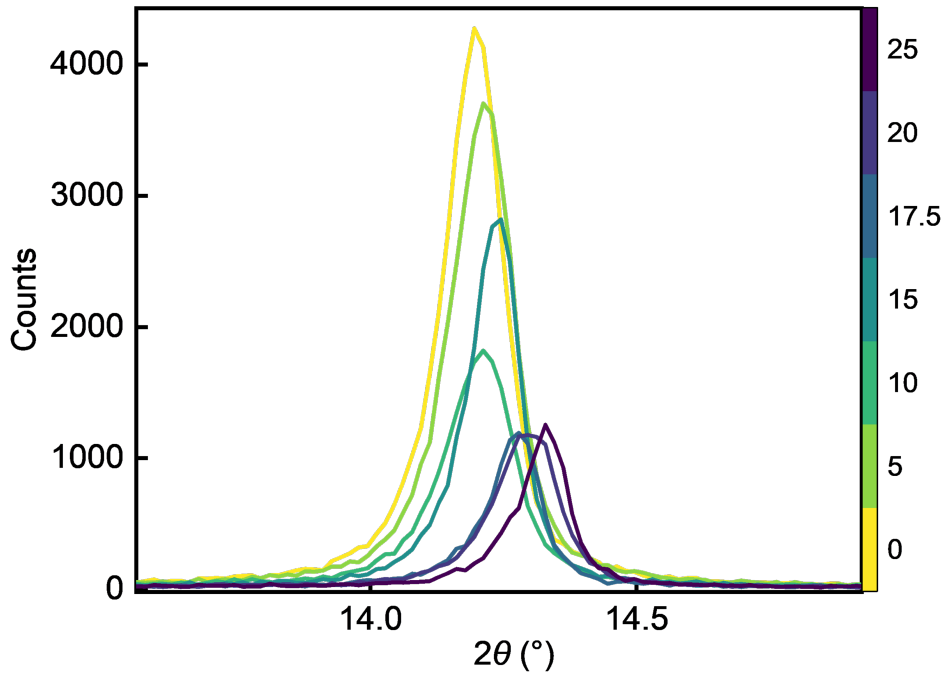


Figure 6.5: XRD patterns of converted $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via 2D templated deposition with increasing Cs incorporation. This figure focuses on the region where the (100) α -phase reflection is observed. The spectra progress from bottom (yellow pattern, pure FA, $y = 0$) to top (purple pattern, 25% Cs, $y = 0.25$).

From 0% to 25% Cs, there is an approximately fourfold reduction in peak intensity. This may indicate that, when films are fabricated via two-step templated processing, the inclusion of Cs can be detrimental to film crystallinity. This behaviour may arise from the increased crystallisation rate in Cs-containing perovskites.^{61,90,91} In such systems, the balance between nucleation and crystal growth is shifted towards rapid nucleation due to the modified crystallisation kinetics introduced by Cs incorporation. If crystallisation proceeds too quickly, this can result in a high density of nuclei, limiting subsequent grain growth and leading to films composed of smaller grains with a higher density of grain boundaries and defects. These structural inhomogeneities reduce the overall crystalline quality and introduce non-radiative recombination pathways, thereby degrading optoelectronic performance.⁹³

Control over this nucleation-growth competition is therefore critical. Reoptimisation of quenching protocols can moderate the effective crystallisation pathway by inducing rapid supersaturation to initiate nucleation, while simultaneously limiting excessive crystal growth. This enables improved grain coalescence and more uniform crystallinity across the film.⁹⁴ Interestingly, the decrease in intensity is relatively consistent between 0% and 15% Cs; however, for higher Cs concentrations, the reflections no longer continue to decrease significantly in intensity. This may suggest that

further process optimisation is required for individual Cs compositions, as otherwise the trend of decreasing crystallinity might be expected to continue rather than plateau. Nevertheless, to enable direct comparison, the fabrication methodology was kept constant for these experiments.

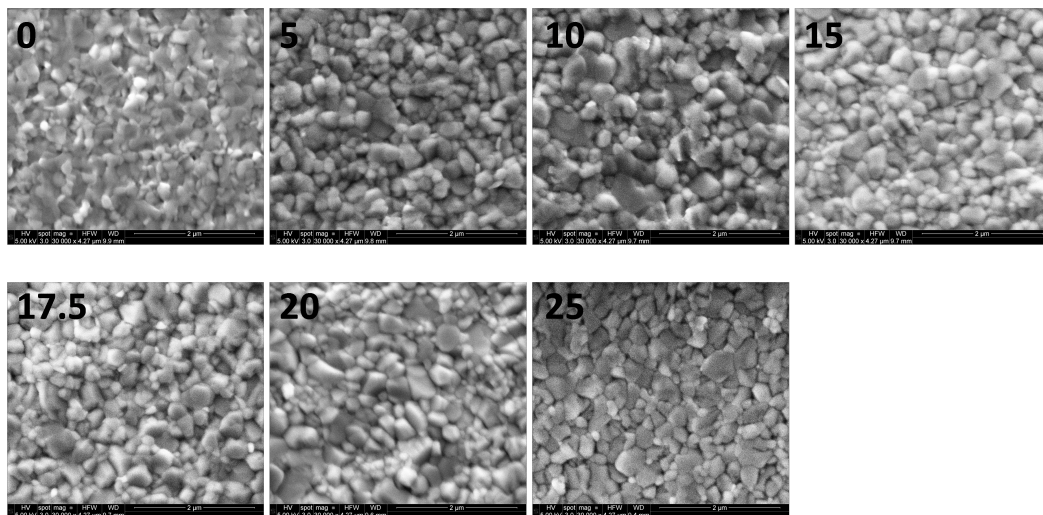


Figure 6.6: SEM images of converted $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via 2D templated deposition with increasing Cs incorporation. From top left (pure FA, $y = 0$) to bottom right (25% Cs, $y = 0.25$).

While the inclusion of Cs in the perovskites appears to be detrimental to the crystallinity of films made via templated processing, SEM images of the same films (shown in Figure 6.6) suggest a different effect on their morphology. For instance, comparing the pure FA film with the 5% Cs film (shown in the first two images of the figure), even a small amount of Cs appears to significantly alter the film morphology. The 5% Cs film exhibits more well-defined and larger apparent grains compared to the neat FA film.

Subsequent films with increasing Cs content retain this improved morphology, with only minor variations, up to 20% Cs. However, the 25% Cs film displays a distinctly different morphology. In this film, the apparent grains appear less densely packed, with small gaps emerging at the grain boundaries. These observations suggest that incorporating 5–20% Cs into the films results in a superior top-surface morphology, although this behaviour may change once the processing is optimised for each composition.

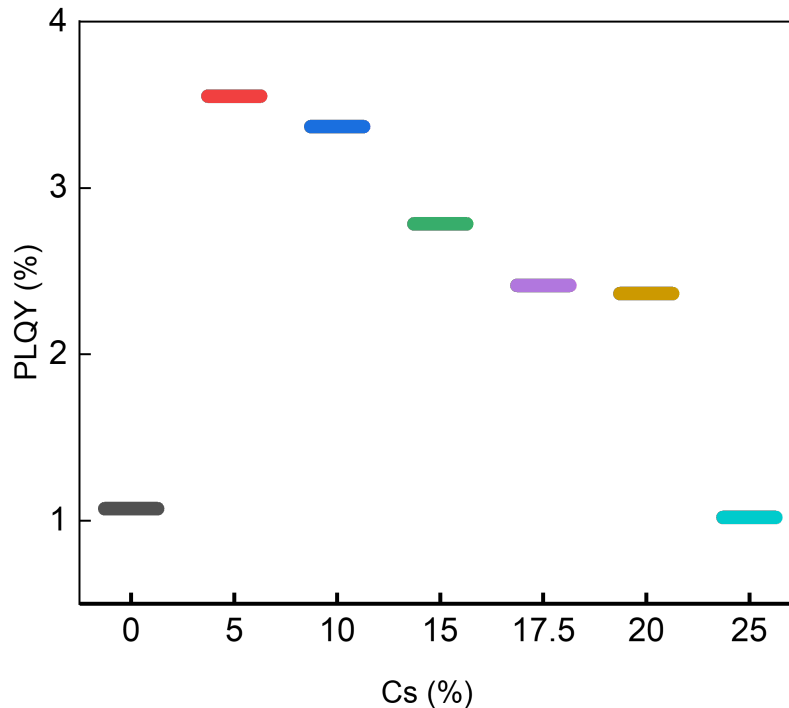


Figure 6.7: Scatter plot of calculated photoluminescence quantum yield (PLQY) measurements (using a 532 nm wavelength laser) for converted $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via 2D templated deposition with increasing Cs incorporation from 0% to 25%.

Spectroscopic measurements were performed to better determine the optimum Cs composition for improved optoelectronic properties. PLQY measurements were first carried out using a 532 nm laser, with the excitation power calibrated to correspond to one-sun intensity. A scatter plot of the calculated PLQY values is shown in Figure 6.7. A clear trend is observed with increasing Cs content. The PLQY increases approximately threefold when the Cs content is raised from 0% to 5%. Thereafter, further increases in Cs content result in a consistent reduction in PLQY, until the value returns to that of the control film at 25% Cs.

As PLQY is commonly used as an indicator of non-radiative recombination in a film, this trend could suggest that small amounts of Cs improve the optoelectronic quality of the perovskite, likely through a reduction in trap density. However, given the different morphology of the samples, this effect could also be related to surface roughness. An increase in surface roughness can enhance outcoupling during PLQY measurements, leading to an apparent increase in PLQY.

If small amounts of Cs do indeed reduce the trap density in the perovskite, this effect may also be reflected in the charge-carrier dynamics. To investigate this, time-resolved photoluminescence (TRPL) measurements were performed on the films, along with steady-state photoluminescence (SSPL) measurements to determine the appropriate excitation wavelengths for each composition. Figure 6.8 shows the SSPL spectra of the films. A similar blue shift to that observed in the UV–Vis absorption spectra is seen as the Cs content increases.

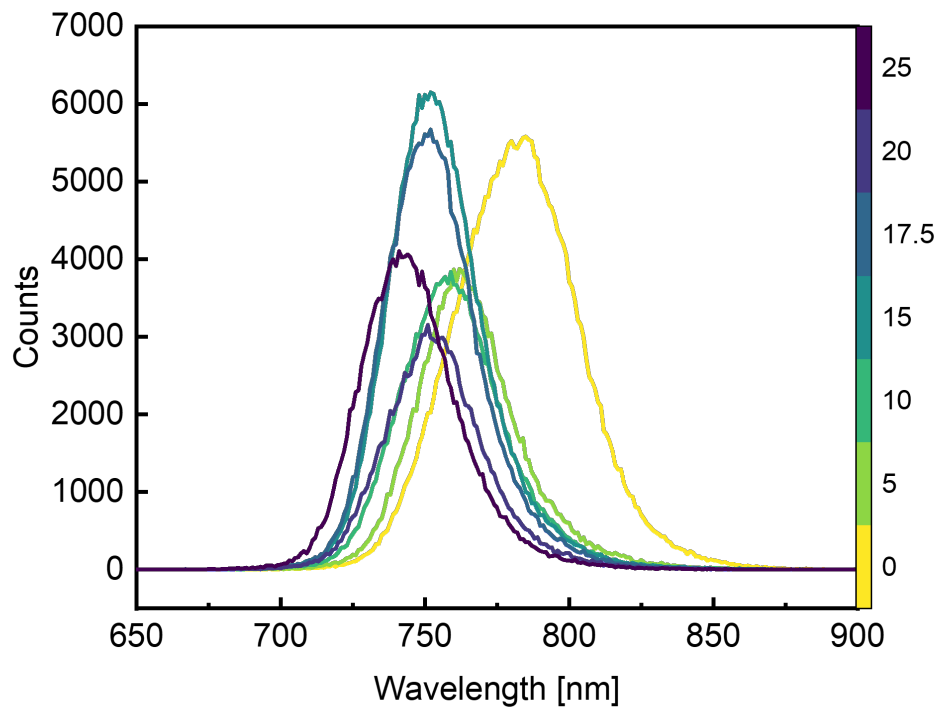


Figure 6.8: Steady-state photoluminescence (SSPL) spectra (using a 532 nm wavelength laser) for converted $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via 2D templated deposition with increasing Cs incorporation from 0% to 25%.

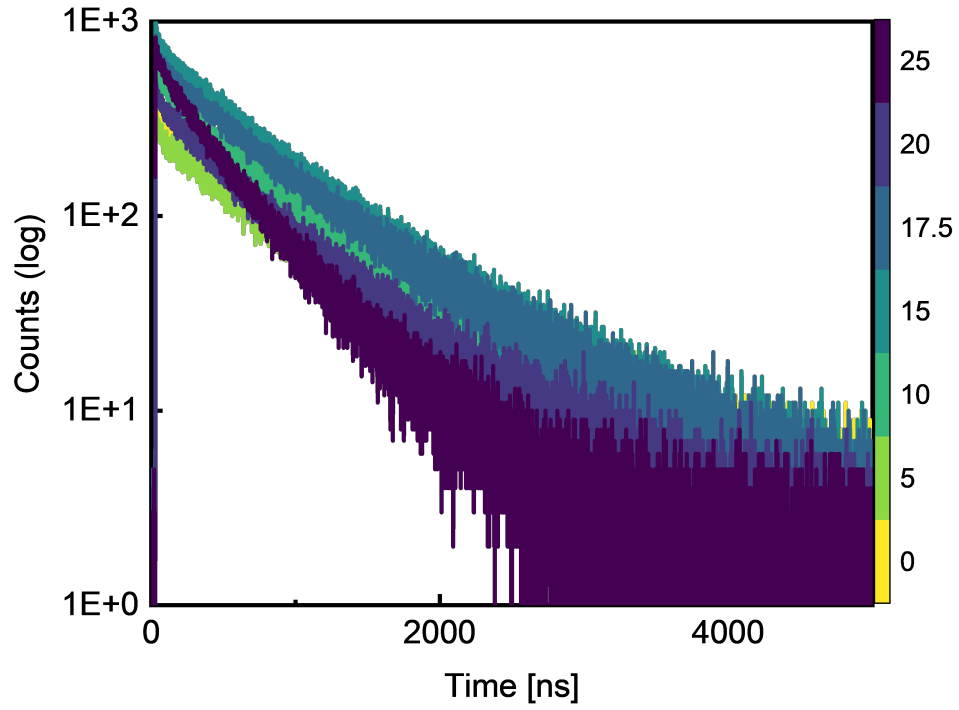


Figure 6.9: Time-resolved photoluminescence (TRPL) spectra (using a 532 nm wavelength laser) for converted $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via 2D templated deposition with increasing Cs incorporation from 0% to 25%.

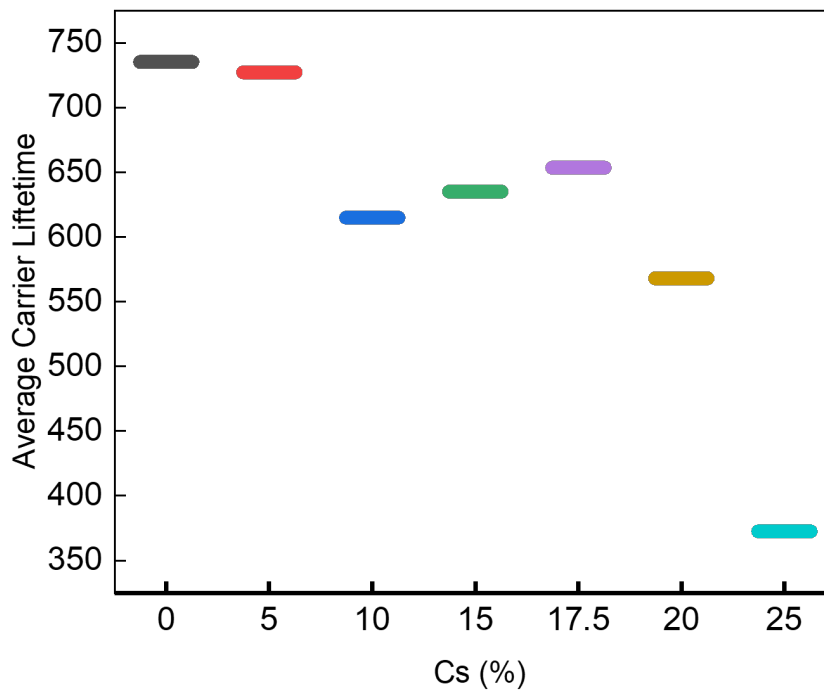


Figure 6.10: Scatter plot of calculated carrier lifetimes (from TRPL measurements) for converted $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via 2D templated deposition with increasing Cs incorporation from 0% to 25%.

Using the peak positions extracted from the SSPL measurements, TRPL measurements were conducted on the samples. The TRPL spectra and a scatter plot of the extracted lifetimes (obtained using a stretched exponential model) are shown below. There is a discrepancy with the trend observed in the PLQY measurements. The Cs-free control sample exhibits the longest calculated charge-carrier lifetime (735.3 ns). There is a slight decrease in the 5% Cs sample (727.2 ns). The 10%, 15%, and 17.5% Cs samples show comparable, but reduced, lifetimes of approximately 630 ns. The shortest lifetime is observed for the 25% Cs sample (372 ns), representing a significant decrease. This consistent trend may suggest that the templated processing has not been optimised for Cs-containing films. This follows from the argument above that Cs containing films, which have not been fabricated with optimised processing can have higher defect densities due to faster crystallisation rates.⁹³

6.3 MATERIAL STABILITY

6.3.1 Impact of Cs

The first stability experiments were conducted to investigate the impact of Cs on the stability of templated perovskites. Until now, the lack of a pure FA mixed-halide perovskite has meant that Cs has been a necessary component of wide-bandgap perovskites. Consequently, a direct comparison of the stability of Cs-free and Cs-containing films has not previously been possible.

In the following section, the material stability of selected perovskite compositions is compared, specifically 0%, 5%, and 17.5% Cs. The 5% composition was chosen because it exhibited the best morphology and optoelectronic properties among the Cs-containing samples. The 17.5% Cs composition was selected because it is commonly used in optimised wide-bandgap device recipes.

The films were spin-coated onto glass substrates and covered with a layer of PMMA. UV–Vis absorption and XRD measurements were taken before ageing. The films were then aged at 85 °C and 85% relative humidity under one-sun illumination for 6 hours. After ageing, the films were remeasured. The XRD diffractograms of each film are shown individually below, followed by the UV–Vis absorption spectra of all three samples overlaid.

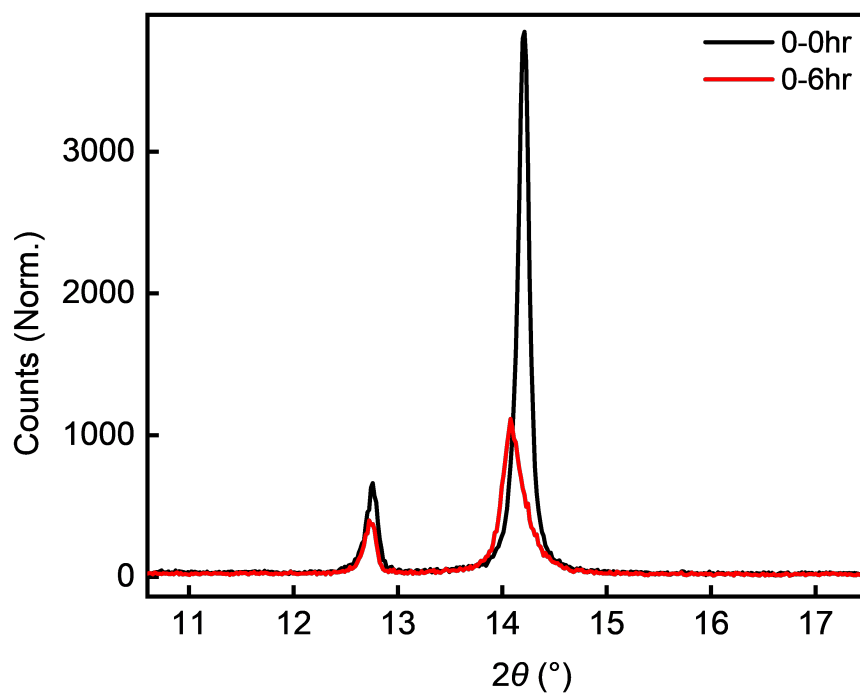


Figure 6.11: XRD diffractogram for 0% Cs-containing $\text{FAPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films before (0 hr) and after ageing (6 hr) at 85 °C and 85% relative humidity under one-sun illumination.

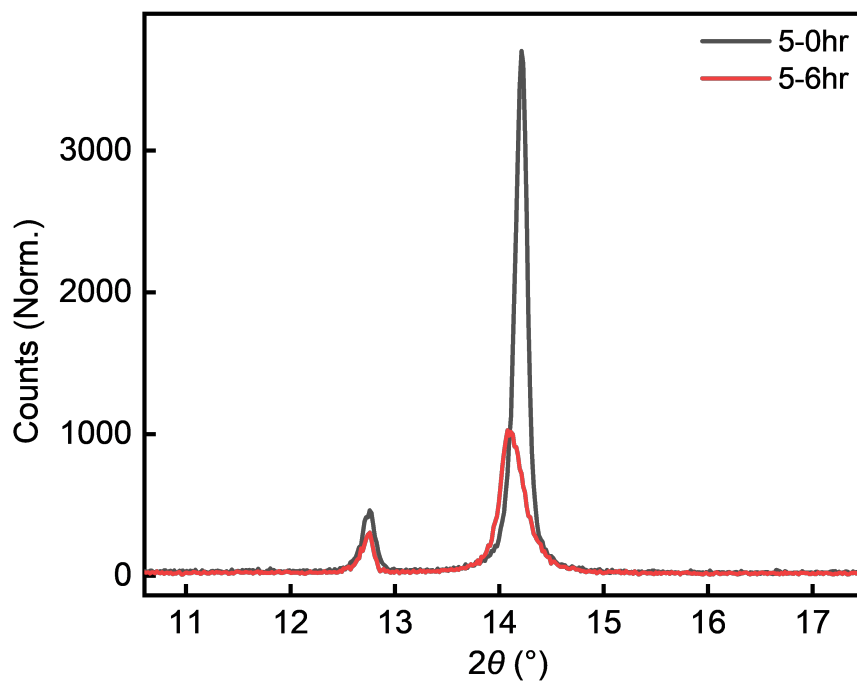


Figure 6.12: XRD diffractogram for 5% Cs-containing $\text{FACsPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films before (0 hr) and after ageing (6 hr) under the same conditions.

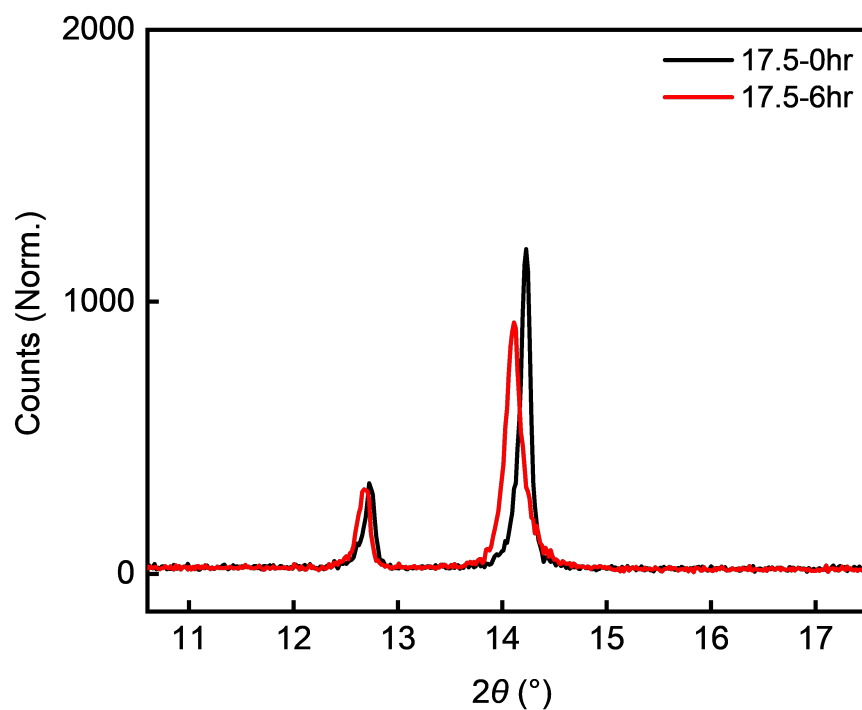


Figure 6.13: XRD diffractogram for 17.5% Cs-containing $\text{FACsPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films before (0 hr) and after ageing (6 hr) under the same conditions.

The XRD data support the observation that films with lower Cs content exhibit higher crystallinity, as the intensity of the (100) reflection prior to ageing is significantly greater in the 0% and 5% samples compared to the 17.5% sample. Following ageing, the intensity of this reflection decreases for all compositions to a similar value (~ 1000 counts), indicating a substantial reduction in crystalline quality⁹⁵. However, the persistence of distinct diffraction peaks suggests that the material remains crystalline, with increased structural disorder rather than complete amorphisation. The shift of the (100) reflection to lower angles is consistent with unit cell expansion and is associated with bandgap narrowing.

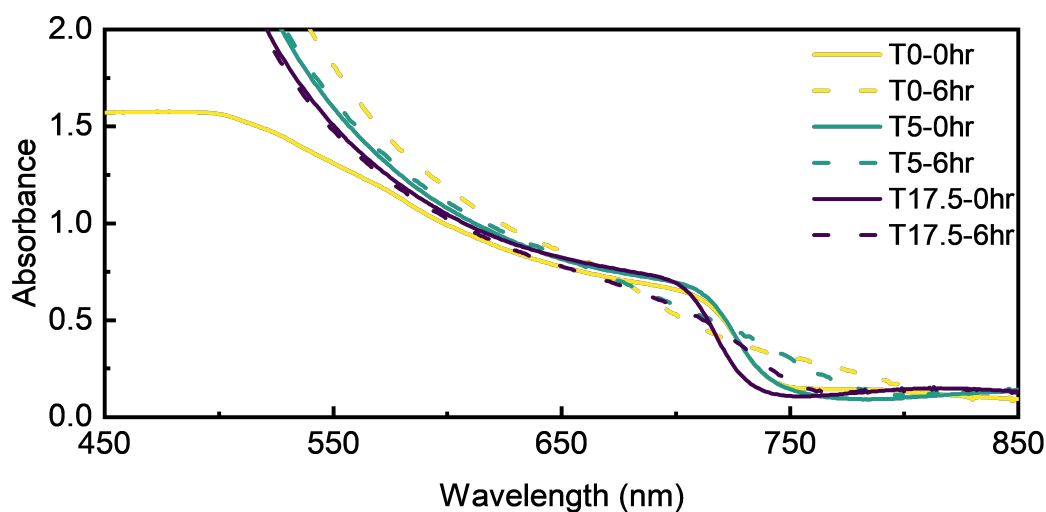


Figure 6.14: UV–Vis absorption spectra for 0%, 5%, and 17.5% Cs-containing $\text{FACsPb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films before (0 hr, solid line) and after ageing (6 hr, dashed line).

This is reflected in the absorption spectra which shows a redshift of the absorption edge after ageing, accompanied by a slight broadening of the onset. This behaviour is consistent with bandgap narrowing arising from compositional changes within the film, most likely iodide enrichment due to halide redistribution or preferential bromide depletion.⁹⁶ However, it is worth noting that iodine-related degradation processes, including iodide migration, defect formation, and I_2 volatilisation, are widely reported in the literature and are often considered a dominant instability pathway in halide perovskites rather than bromide-loss.^{97–99}

This data closely resembles the XRD and absorption spectra of semi-crystalline materials within the miscibility gap observed for unsuccessful processing methods, such as the MeTHF/BA system. This supports the hypothesis that the aged films consist of a mixture of crystalline and

amorphous material.

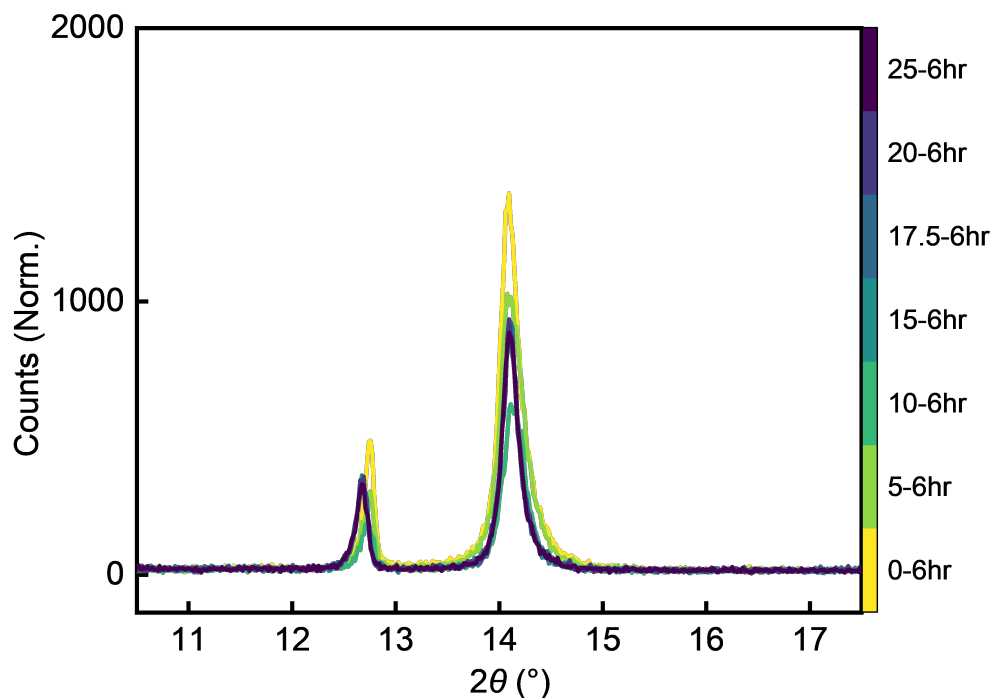


Figure 6.15: XRD patterns of aged converted $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via 2D templated deposition with increasing Cs incorporation. The spectra focus on the (100) α -phase reflection.

To determine whether there is any discernible difference in stability due to Cs content, the XRD diffractograms of all films are shown in Figure 6.15. This figure suggests that the control film is slightly more crystalline than the Cs-containing films after ageing, as the reflection intensity is greater. However, this may simply reflect the initially higher intensity of the control film due to optimised processing. Overall, the reflection intensities of all films converge to a similar level after ageing.

Although these results suggest that Cs content does not significantly impact the degradation rate, and therefore may not improve stability, this conclusion is not robust. It is possible that the processing method produces metastable films that degrade rapidly under photothermal stress, and that the processing is not optimised for Cs-containing films.

6.3.2 Impact of Templating

As mentioned in the introduction, the stability of the α -phase in mixed A-site perovskites is directly influenced by the homogeneity of A-site cation mixing. To investigate whether 2D-templated processing improves the stability of perovskite films, a direct ageing comparison was conducted between conventionally processed one-step films and templated films of composition $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$.

The UV–Vis absorption spectra shown in Figure 6.16 indicate that, while both films exhibit sharp absorption onsets prior to ageing, the templated film shows a greater reduction in absorption sharpness after ageing. Both films also exhibit a red shift in the absorption onset; however, this effect is more pronounced in the templated films.

These results suggest that the initial hypothesis, that templating would improve film stability due to enhanced compositional homogeneity, may not hold. It is possible either that the templated films do not exhibit improved A-site mixing as anticipated, or that an additional degradation pathway is present in the templated films but not in the one-step processed films.

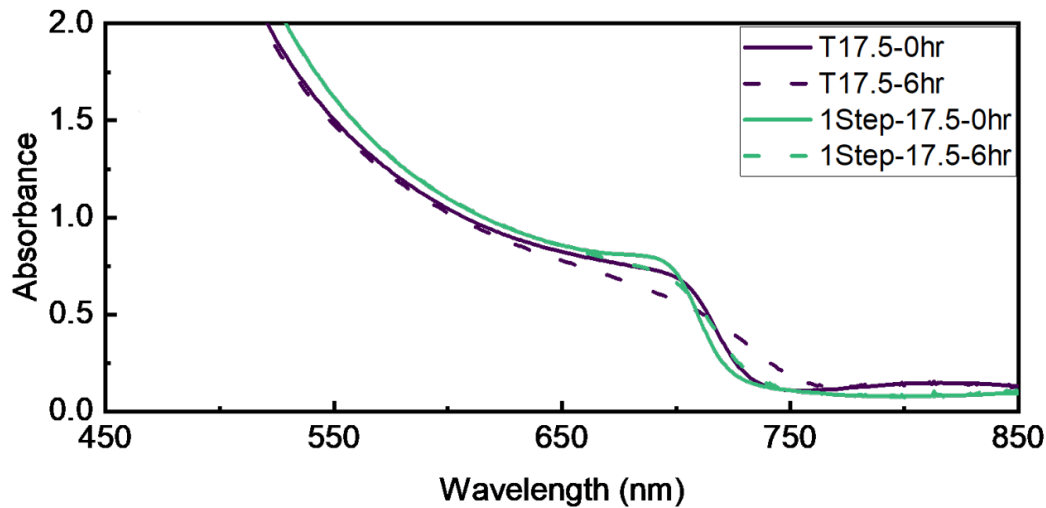


Figure 6.16: UV–Vis absorption spectra of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ films made via templated and one-step processing before and after ageing.

6.3.3 Ruddlesden–Popper Templates

In order to improve the stability of the 2D-templated films, the processing method itself was reconsidered. For instance, the mixture of 2D and 3D phases within the template may influence the stability of the final film. Referring to the argument in Chapter 5, the preferential allocation of halides within the 2D template enables the formation of lead halide octahedra, which stabilise the α -phase. This may provide some insight into how the processing could be improved.

It is possible that this allocation of halides to specific sites is more homogeneous and ubiquitous in pure $n = 2$ Ruddlesden–Popper films than in mixed 2D/3D templates. Therefore, employing a pure 2D template may further stabilise the final film. Even though these templates were previously abandoned due to delamination issues, they are reconsidered here to test the proposed theory. Below are the XRD diffractograms for the films prepared from pure 2D (labelled RP) templates before and after aging. UV–Vis absorption spectra were also collected for the pure FA films prepared using both mixed 2D/3D (labelled 1:1) and pure 2D (labelled RP) templates, before and after aging.

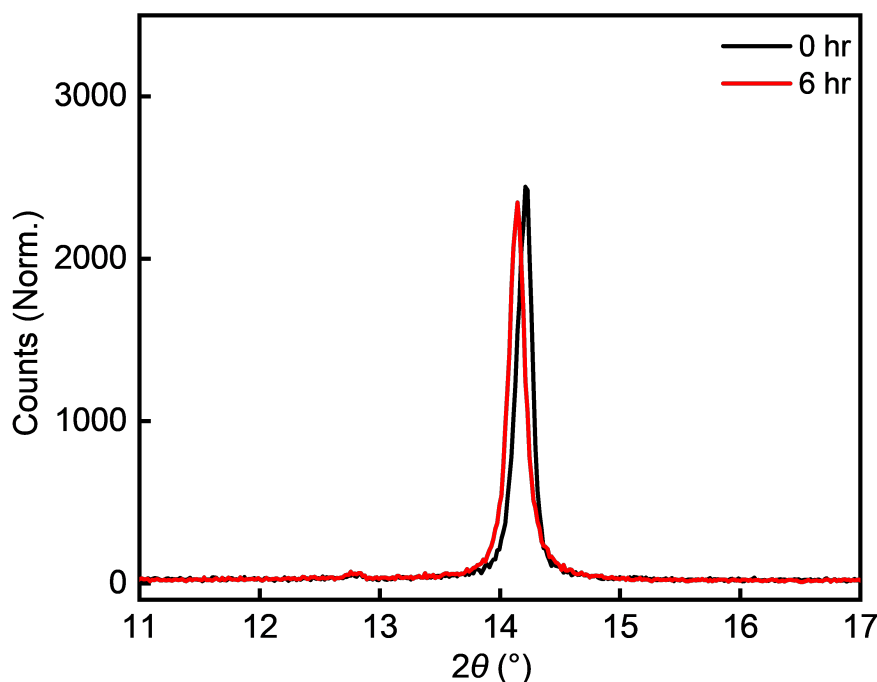


Figure 6.17: XRD diffractogram for pure 2D templated films before and after ageing.

The XRD pattern for the 2D-templated films shows significantly less loss in intensity of the (100) reflection compared to the mixed 2D/3D-templated films shown in Figure 6.17. This may indicate reduced loss of crystallinity due to amorphisation. Although the initial intensity of the pure 2D-templated films is slightly lower, it remains comparable to that of the mixed 2D/3D-templated films, suggesting that these conclusions remain valid. However, a shift in the reflection to lower angles is still observed, indicating that, while amorphisation may be reduced relative to the mixed 2D/3D-templated films, it is not entirely suppressed.

The UV–Vis absorption spectra in Figure 6.18 also corroborate these claims. While both films exhibit some loss of sharpness in their absorption onset, the effect is more pronounced in the films made from mixed 2D/3D templates. However, despite these improvements in material stability, changes are still observed in both the XRD and UV–Vis data, suggesting that the films remain metastable. It would be interesting to investigate whether the impact of Cs on these films differs from that observed in the mixed 2D/3D-templated films; however, this would require further study.

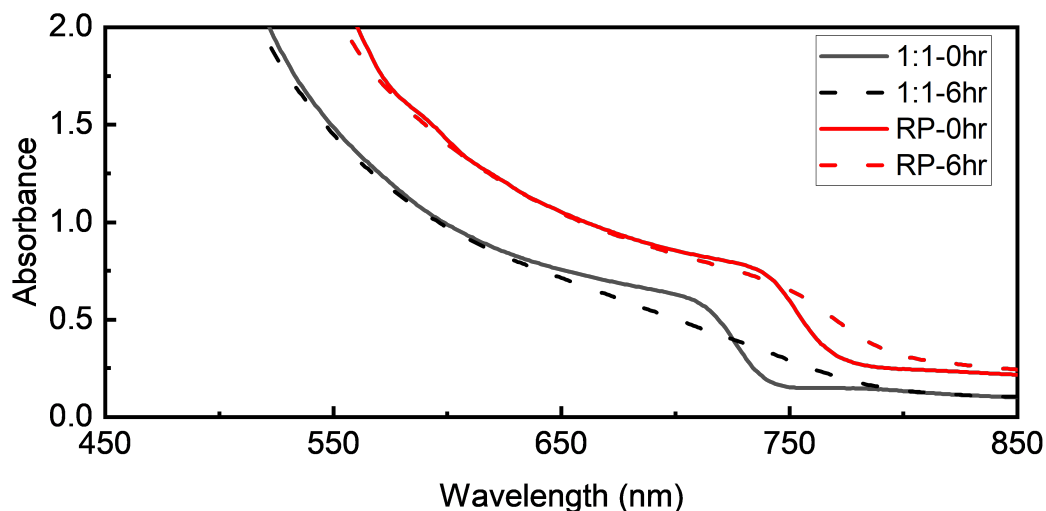


Figure 6.18: UV–Vis absorption spectra comparing pure 2D and mixed 2D/3D templates before and after ageing.

6.4 CONCLUSION

The purpose of the investigations in this chapter was to compare the impact of templated processing with that of Cs incorporation on the stability of perovskites. In this chapter, Cs has been successfully incorporated into the templated processing. However, results from the majority of the optoelectronic characterisation suggest that Cs has a detrimental impact on the quality of the perovskite films. It is more likely that the processing is not yet optimised for Cs-containing films, rather than this representing a true underlying trend.

Moreover, Cs appears to have little influence on the stability of the templated films, as the films undergo a consistent loss in crystallinity during ageing regardless of Cs content. This suggests that the films are only metastable and that a different degradation pathway, specific to templated films, is dominant.

The second set of investigations assessed the impact of templating on film stability. It is apparent that conventionally processed one-step films exhibit superior stability under photothermal stress, which is consistent with the stability challenges associated with templated films shown in this chapter. Replacing mixed 2D–3D templates with purely 2D templates was explored as a strategy to improve film stability. While this modified processing route did yield some improvement, evidence of amorphisation remains.

Ultimately, it appears that, before either stability question can be fully resolved, a detailed understanding of the degradation pathway in templated films is required. With this understanding, a revised processing method with enhanced stability could be developed, allowing the original questions regarding the roles of Cs incorporation and templating to be more definitively addressed.

CONCLUSIONS AND OUTLOOK

Metal halide perovskites continue to attract considerable interest because of their tunable bandgaps and, in the case of FA-based compositions, their improved thermal stability relative to MA-based compositions. These properties make them highly attractive candidates for single- and multi-junction photovoltaic applications. However, for many years, the practical use of FA-based mixed-halide perovskites was limited by the difficulty of crystallising the photoactive α -phase across the full composition range using conventional one-step processing. This compositional limitation, commonly referred to as the miscibility gap, has shaped much of the subsequent development of these materials.

This thesis has reproduced the miscibility gap experimentally and proposed a physical explanation for its origin using machine-learning interatomic potentials. Rather than arising from an intrinsic instability of the α -phase alone, the miscibility gap is shown to reflect a near-degeneracy in the Gibbs free energy of the α - and δ -phases over an intermediate bromide composition range. This interpretation is consistent with the main experimental observations reported in the literature and provides a more complete description of the phase behaviour of FA-based mixed-halide perovskites.

A major outcome of this work has been the development of a templated crystallisation strategy that enables phase-pure α -FAPb(I_{1-x}Br_x)₃ to be obtained across the full iodide–bromide composition range. Using butylammonium-based mixed 2D/3D templates prepared through an optimised antisolvent route, the miscibility gap was successfully bypassed. Computational modelling suggests that the 2D template stabilises mixed halides through site-selective ordering on inequivalent

halide sites, while elevated-temperature conversion preserves the halide framework during cation exchange. This combination of thermodynamic preference in the template and kinetic trapping during conversion provides a persuasive explanation for why templated processing succeeds where direct crystallisation does not.

The resulting films were shown to possess strong optoelectronic properties. In particular, the 30% bromide composition exhibited excellent charge-carrier mobility and could be incorporated into photovoltaic devices, demonstrating that these materials are viable absorbers even in the composition range that was previously inaccessible. Although the device performance did not reach state-of-the-art values, the work establishes a clear route by which further optimisation could be pursued.

The final part of this thesis examined whether the benefits of templated processing extend to mixed A-site compositions and whether Cs incorporation improves film stability. Cs was successfully incorporated through templated processing, but the resulting films did not show any improvement in stability. Indeed, the available evidence suggests that the templated films remain metastable and that their degradation behaviour is governed by a process distinct from that of conventionally processed films (which were more stable). This suggests that a fuller understanding of the degradation pathway is required before the stability of these materials can be meaningfully improved. Some planned investigations are outlined below.

Firstly, it is crucial to understand the compositional changes in the perovskites under photothermal stress. In particular, X-ray photoelectron spectroscopy (XPS) will be used to identify compositional changes during degradation and determine which elements are lost from the films during ageing tests. This will help clarify the specific degradation mechanisms. This will be supported by in situ photoluminescence (PL) measurements, which will help distinguish whether performance losses arise from halide segregation or from structural amorphisation of the perovskite lattice.

The role of the bottom interface will also be investigated in more detail. It is clear from the spectroscopic measurements that there is asymmetric trapping of charge carriers, which may be limiting device performance. Probing this interface will help to identify the phases formed during processing and clarify the mechanisms responsible for improved film adhesion in the templated structures.

Furthermore, a number of additional investigations will be conducted on the films, building on previous work on one-step FACs systems. In particular, the resistance of the films to A-site mixing

and halide segregation will be examined. Established methodologies from previous studies will be applied, making this a relatively straightforward but informative set of investigations.^{39–42}

To improve device performance, the incorporation of MACl as an additive in the conversion process will be explored, as it has been shown to enhance crystallinity and efficiency in related two-step perovskite systems.¹⁰⁰

Finally, the integration of these templated perovskite films into silicon–perovskite tandem solar cells will be investigated, with the aim of assessing their suitability for high-efficiency multi-junction photovoltaic applications.

Overall, this thesis has answered several of the questions that motivated the work. It has provided a comprehensive explanation for the miscibility gap, demonstrated a general templated route to FA-based mixed-halide perovskites across the full composition range, and shown that these materials can function successfully in photovoltaic devices. At the same time, it has also highlighted that the stability of templated films remains an open question. Further work is therefore needed to clarify the degradation mechanisms of these systems and to determine how best to combine compositional control, templating, and stability in a single processing route.

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- P. Caprioglio, **S. Choudhary**, J. A. Smith, R. D. J. Oliver, A. Dasgupta, M. D. Farrar, *et al.*, “Open-circuit and short-circuit loss management in wide-gap perovskite p–i–n solar cells,” *Nature Communications*, 14, 932 (2023).
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