

Strain Analysis and Engineering in Halide Perovskite Photovoltaics

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Abstract

Halide perovskites are a compelling candidate for the next generation of clean energy harvesting technologies thanks to their low cost, facile fabrication and outstanding semiconductor properties. However, photovoltaic device efficiencies are still below practical limits and long-term stability challenges hinder their practical application. Current evidence suggests that strain in halide perovskites is a key factor in dictating device efficiency and stability. Here, we outline the fundamentals of strain within halide perovskites relevant to photovoltaic applications and rationalize approaches to characterize the phenomenon. We examine recent breakthroughs in eliminating the adverse impacts of strain, enhancing both device efficiencies and operational stabilities. Finally, we discuss further challenges and outline future research directions for placing stress and strain studies at the forefront of halide perovskite research. An extensive understanding of strain in halide perovskite is needed, which would allow effective strain management and drive further enhancements in efficiencies and stabilities of perovskite photovoltaics.

28 Halide perovskites have been thrust into the limelight in the last decade as a promising next-
 29 generation photovoltaic technology, with power conversion efficiencies (PCEs) already
 30 comparable with those of crystalline silicon devices. Reductions in unwanted energy losses
 31 both in the absorber and at interfaces with contact layers have led to substantial efficiency and
 32 stability improvements. Recently, strain control has been at the forefront of device efficiency
 33 enhancement in halide perovskites by minimizing undesirable defect formation^{1,2}, and
 34 subsequent nonradiative recombination³. A certified PCE of ~24.4% has recently been reported
 35 for FAPbI₃-based devices (FA=formamidinium) through managing strain, with the
 36 encapsulated devices retaining 90% of their efficiencies after 400 hours at maximum power
 37 point¹. Such encouraging achievements suggest that strain engineering is a powerful tool to
 38 enhance efficiencies and stabilities for a broad range of practical applications. Despite such
 39 successes, there is an apparent paradox whereby similarly strained halide perovskites exhibit
 40 either beneficial or detrimental effects even when they are nominally similar materials.
 41 Furthermore, the magnitude of strain is relatively high in halide perovskites compared to other
 42 photovoltaic systems: for instance, residual strain values of up to ~2.4% for α -FAPbI₃⁴ and
 43 ~1.6% for CsPbBr₃ have been reported⁵, whereas the performance of Si and Cu(In, Ga)Se₂
 44 devices drops substantially when residual strains exceed ~1%^{6,7}. The high magnitude of strain
 45 in perovskite materials is particularly striking since perovskites are one of the most
 46 mechanically fragile of any photovoltaic materials⁸. It is therefore essential to thoroughly
 47 understand the fundamentals of strain on different length scales, and to devise effective
 48 methods to characterise it. This will allow us to move towards rational engineering as opposed
 49 to empirical optimisation.

50 1. Definition and measurement of strain in halide perovskites

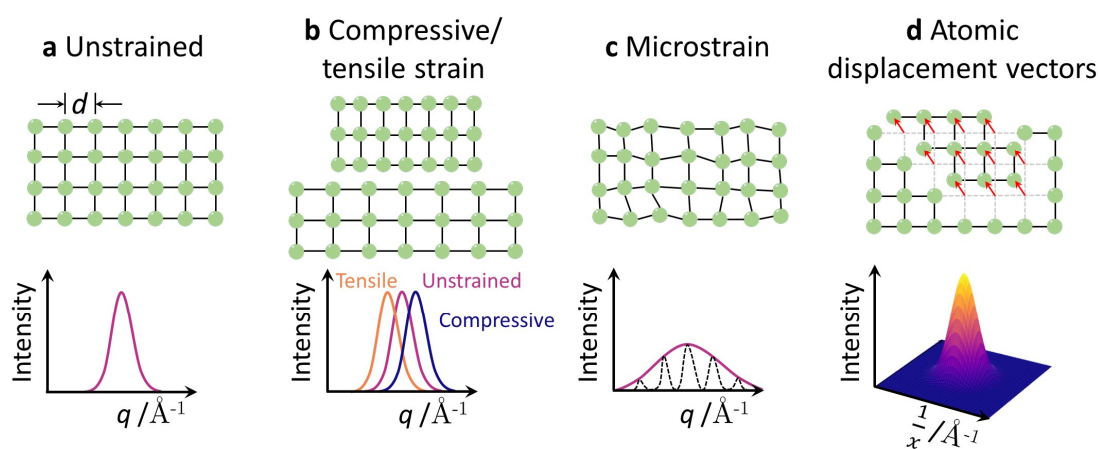
51 Strain (ϵ) is defined as a structural deformation of a material in response to applied stress(σ)⁹.
 52 This stress can be from external forces on the material, or internal structural defects such as
 53 atomic interstitials and vacancies. Mathematically, strain is defined by a (second rank) tensor
 54 with elements given by

$$55 \quad \epsilon_{kl} = \frac{1}{2}(e_{kl} + e_{lk}) .$$

56 Here, $e_{kl} = \frac{\partial u_k}{\partial x_l}$, where u_k are the components of the atomic displacement vector $\mathbf{u}(x_1, x_2, x_3)$
 57 along the Cartesian directions, and x_l are the Cartesian coordinates. $\mathbf{u}(x_1, x_2, x_3)$ describes the
 58 displacement of atoms from their expected positions in an unstrained material, and the above
 59 definition is valid for small displacements. This particular linear combination of $\frac{1}{2}(e_{kl} + e_{lk})$
 60 removes the effects of rigid rotation from the strain tensor¹⁰. Determination of this tensor
 61 constitutes a full description of strain in materials as the atomic displacement vectors can be
 62 reconstructed from the tensor elements. Such a description not only encapsulates the length
 63 changes along the Cartesian axes given by $\epsilon_{x_1x_1}$, $\epsilon_{x_2x_2}$, and $\epsilon_{x_3x_3}$, but also the shear
 64 components of the deformation given by the off-diagonal elements. In the elastic regime, the
 65 magnitude of the deformation resulting from the applied stress (also a tensor, σ) can be

66 calculated from Hooke's law, $\sigma_{ij} = c_{ijkl}\epsilon_{kl}$, where c_{ijkl} are the components of a (fourth rank)
 67 stiffness tensor.

68 The aspects of strain in a material that can be determined with typical laboratory techniques
 69 include tensile and compressive strain where the interplanar spacing, d , of the material is
 70 compared to a reference "unstrained" value. Typically, the variation in d spacing is observed
 71 through the Bragg peak positions in an X-ray diffraction (XRD) pattern. If a material is
 72 compressively strained, the d spacing is decreased relative to the reference, and the peak
 73 associated with that plane will shift to higher scattering vector, \mathbf{q} (Fig. 1a,b), with the converse
 74 being true for tensile strain. The values of compressive/tensile strain are usually expressed as
 75 a ratio of the d spacings and written as percentages. The nature of strain (compressive/tensile)
 76 is indicated either explicitly or using a negative/positive sign indicating compressive/tensile
 77 strain, respectively. However, we note that such measurements only probe the diagonal (ϵ_{kk})
 78 elements of the strain tensor. Furthermore, applying a load (stress) to a material results in
 79 deformations (strain) not only in the directions parallel to, but also perpendicular to the load
 80 (Poisson's effect). For example, a biaxial in-plane tensile strain in a halide perovskite thin film
 81 will also result in a compressive strain in the direction of the film normal¹¹. This is especially
 82 pertinent because many lab-based X-ray diffractometers are in Bragg-Brentano (reflection)
 83 geometry with the scattering vector in the direction of the film normal. Consequently, it is the
 84 out-of-plane compressive strain that will be probed.



85

86 **Fig. 1| Definition and measurement of strain in halide perovskites. a-d,** The top row gives
 87 representations of (a) unstrained material, (b) compressive/tensile strain, (c) microstrain, and
 88 (d) atomic displacement vectors. The bottom row indicates the signatures of each of these kinds
 89 of strain in diffraction patterns.

90 An additional feature of strain reported is "microstrain" which is determined by Bragg peak
 91 width analyses. If the diffraction measurement simultaneously samples a number of different
 92 d spacings within the sample, then contributions from all these d spacings will combine to
 93 form a broadened Bragg peak (Fig. 1c). Microstrain is a measure of local deviations of d
 94 spacings from their average value and includes contributions from both locally compressively
 95 and locally tensile strained regions. A commonly employed method for calculating microstrain

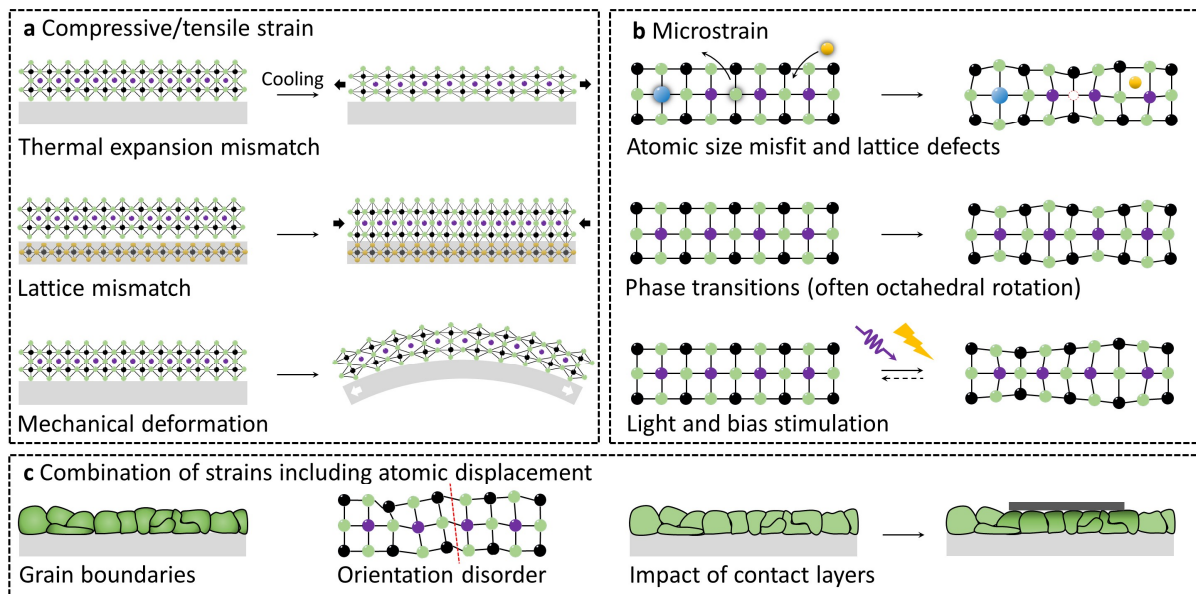
96 is Williamson-Hall analysis¹². The method relies on the different q -dependence of Bragg peak
97 broadening resulting from microstrain and crystallite size effects and, despite the method's
98 ubiquity, there are many potential pitfalls. One must first remove any instrument broadening,
99 which is typically accomplished using an external standard, but these standards may not be in
100 the same form as the sample (e.g. thin film) and thus do not exactly reproduce the conditions
101 of the diffractometer for the sample. Further, many nuances influence the crystallite size
102 calculation including the distribution of sizes, shape, and crystallite length in each
103 crystallographic direction. Errors in calculation of particle size will have a knock-on effect for
104 determination of microstrain. Depending on the structural features (dislocations, variable
105 lattice distortion, grain surface relaxation) there may or may not be a strong hkl dependence
106 on microstrain peak broadening, which complicates matters further. Therefore, the researcher
107 must be especially diligent when carrying out peak broadening analyses from lab-based bulk
108 XRD measurements¹². We also stress that microstrain values are not directly comparable to
109 compressive/tensile strain values given that these two quantities probe different aspects of
110 material structure. The community must avoid interchangeable use of these terminologies to
111 prevent errors.

112 Another important consideration is the relevant length scale of the measurement. All of the
113 lattice planes that satisfy the Bragg condition within the sample interaction volume (defined by
114 the footprint and penetration depth) of the X-rays contribute to a given diffraction peak. In
115 most lab-based X-ray diffractometers, the beam footprint is on the scale of millimetres squared
116 and so the interaction volume is large and variations in d spacings in this region result in a
117 broadened Bragg peak. However, by reducing the beam footprint and scanning the illumination
118 position across the sample, the local shifts in d spacing can be resolved in the form of a tensile
119 and compressive strain map. This forms the basis for spatially resolved XRD techniques
120 (micro- or nano-XRD) that are able to measure local peak shifts or phase changes³. Overall,
121 one must consider the relevant length scales to probe in halide perovskites given that
122 heterogeneities are present over nanometers up to many micrometers¹³.

123 Other advanced techniques are required to probe beyond the diagonal elements of the strain
124 tensor corresponding to structure expansion/contraction. By using the three-dimensional
125 intensity distribution around Bragg peaks, one can reconstruct the electron density of a crystal
126 to find the atomic displacement vectors (Fig. 1d) from which the off-diagonal components of
127 the strain tensor can be extracted. Techniques that can provide such rich information even on
128 the local scale include Bragg coherent diffraction imaging and Bragg ptychographic
129 approaches^{14, 15}.

130 **2. Origins of strain in halide perovskites**

131



132

133 **Fig. 2| Origins of strain in halide perovskites. a-c,** Representations of the origins of (a)
 134 compressive/tensile strain, (b) microstrain, and (c) more complex strain (including
 135 contributions from shear and rotational components of the strain tensor) in halide perovskites.
 136 The blue and purple spheres are the A-site cations (e.g., Cs, MA and FA), and the black and
 137 green spheres represent metal cations (e.g., Pb, Sn) and halide anions (e.g., Cl, Br and I),
 138 respectively. In a, the orange spheres are substrate atoms. In (b), the red dashed circle is a
 139 vacancy, and the yellow sphere represents the extrinsic dopant that causes a defect. The red
 140 dashed line in (c) indicates a twin boundary.

141 Strain can result from a broad range of factors. During film formation, the precursor solutions
 142 are deposited on a substrate and the film is annealed (often above 100 °C). If the film is formed
 143 on a substrate with a lower coefficient of thermal expansion (CTE) than the perovskite ($3.3\sim 8.4$
 144 $\times 10^{-5} \text{ K}^{-1}$)¹⁶, the substrate restricts the contraction of the perovskite along the in-plane
 145 directions during cool down¹⁷, resulting in an in-plane tensile strain (Fig. 2a, top). Analogously,
 146 compressive strain can occur in a film grown on a substrate with a higher CTE than that of the
 147 perovskite, though this is less common in halide perovskite devices. This process of cooling
 148 after annealing leads to strain (generally tensile) in the plane of the film.

149 Lattice mismatch between the substrate and the as-formed perovskite film can also generate a
 150 tensile or compressive strain (Fig. 2a, middle), depending on whether the *d* spacing of the
 151 substrate is larger or smaller than that of the perovskite overlayer. However, when the lattice
 152 mismatch is large, the perovskite crystal randomly stacks on the bottom crystal, resulting in a
 153 non-uniform interfacial distortion^{18, 19}. Compressive and tensile strains can also be introduced
 154 to films using mechanical film bending²⁰ (Fig. 2a, bottom) and hydrostatic pressure²¹.

155 While the above factors generally influence strains across the whole film, other factors
 156 including atomic misfits, phase transitions, light/bias stimulation and grain boundaries are
 157 linked to local strain (namely microstrain) in halide perovskites (Fig. 2b). For example, in
 158 FAPbI₃, the large FA cation within the 3D structure promotes local PbI₆ octahedral tilting (that

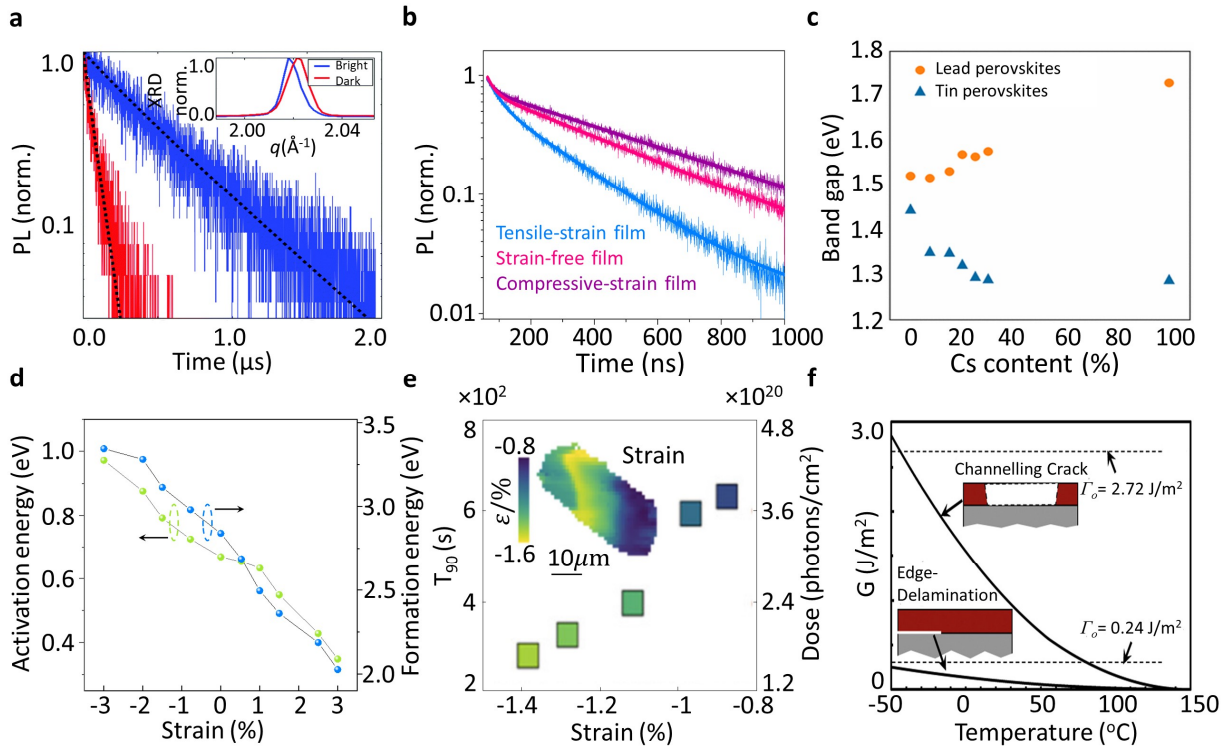
159 is, the Pb-X-Pb angle deviates from the ideal 180°), resulting in a local lattice distortion^{2, 22}.
160 Further, local lattice distortion and strain are greatly elevated during phase transitions, where
161 the symmetry of the crystal structure is generally lowered compared to the cubic perovskite
162 structure. Group theoretical analysis²³ of octahedral tilting schemes yields group-subgroup
163 relationships between perovskite phases (e.g. $I4/mcm$ is a subgroup of $Pm\bar{3}m$) which can
164 transform in a continuous (i.e., second-order) fashion, leading to spontaneous strains due to
165 continuous lattice parameter variation between phases upon octahedral tilting²⁴⁻²⁶. Large strains
166 and complex microstructure, such as martensitic nano/microstructures²⁶ or crystal twins, can
167 result from discontinuous (i.e., first-order) phase transitions with abrupt changes in lattice
168 parameter, which can occur between non-group-subgroup related space groups (though first-
169 order transitions between group-subgroup phases are also possible). Such a transition is found
170 in MAPbI₃ (MA = methylammonium) between $I4/mcm$ to $Im\bar{3}$, at a hydrostatic pressure of
171 ~ 0.3 GPa²¹. Martensitic transformations are diffusionless and often involve a lowering of
172 crystal symmetry (e.g., from cubic to tetragonal²⁷) and when the resulting phases are mutually
173 spatially constrained, strain minimisation can result in a change in shape and curvature of their
174 interface²⁸. Therefore, one can use strain to vary the nano/microstructure resulting from
175 martensitic transformations, as has been shown, for example, in SrSnO₃²⁹. Given the
176 prevalence of symmetry lowering phase transitions in halide perovskites, a more detailed
177 understanding of the strains resulting from phase transitions will be beneficial.

178 Photovoltaic devices are exposed to light and bias during operation, and these have been
179 reported to affect microstrain in halide perovskites. Recently, it was suggested that microstrain
180 is enhanced under illumination owing to light-assisted ion migration and/or phase segregation³⁰.
181³¹. Here, it was proposed that photoexcited carriers within perovskites interact with the soft,
182 ionic lattice^{32, 33}, resulting in greater microstrain. Further, some works attempt to probe the
183 links between photo-induced lattice expansion and microstrain (excluding the effect of ion
184 migration), but debate is ongoing^{34, 35}. Under illumination, the polarity (positive or negative)
185 and magnitude of bias voltages have also been reported to be critical in inducing microstrain
186 by enhancing ion migration³⁰.

187 Grain boundaries can be another source of strain in halide perovskites (Fig. 2c, left) with the
188 resulting strain dependent on the specific interfacial conditions, e.g., orientation mismatch at
189 boundaries³⁶, of which there is striking variation within thin films. It has been proposed that
190 defect formation at certain grain boundaries in perovskite thin films stems from asymmetric
191 strain fields at junctions between grains³⁷. The high degree of lattice distortion and non-
192 stoichiometric chemical distribution at grain boundaries also cause large strain fields^{3, 38}. Apart
193 from boundaries between grains, sub-grain lattice orientation disorder³⁶ (Fig. 2c, middle) and
194 twin boundaries may also be sources of strain in halide perovskite films³⁹. Contact layers are
195 also known to exert forces on the adjacent perovskite films in devices, however, we note that
196 this is highly dependent on the thickness and stiffness of contact layers (Fig. 2c, right)^{20, 40}.
197 Given the substrate's comparatively larger thickness, the substrate will dominate in imparting
198 strain in perovskite devices²⁰.

199 3. The effects of strain on halide perovskites

200 Strain affects the structure of halide perovskites and consequently influences the optoelectronic
 201 properties and stability of the material, which both need to be optimised to push perovskite
 202 devices towards commercialization.



203

204 **Fig. 3| Effects of strain on halide perovskites.** **a**, Time-resolved photoluminescence (PL)
 205 decays for differently strained regions of a MAPbI₃ film where the PL lifetime in the more
 206 compressively strained region (red; dark PL) is shorter than that in the more tensile strained
 207 region (blue; bright PL). Inset: 220 Bragg peaks show the difference in lattice spacing for the
 208 two regions. **b**, Time-resolved PL decays for three (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} films with
 209 different strains. **c**, The variation of bandgap with Cs content (scales with lattice parameter) for
 210 FA_{1-x}Cs_xPbI₃ (orange circles) and FA_{1-x}Cs_xSnI₃ (blue triangles). **d**, Calculated strain-dependent
 211 activation energies of ion migration and formation energies of halide vacancies in CsPbI₂Br
 212 where the minus/plus values in the *x*-axis represent compressive/tensile strain, respectively. **e**,
 213 Time for the XRD pattern correlation coefficient to decay to 90 % of its original value (*T*₉₀)
 214 against strain. The right *y*-axis shows the sample's radiation dose. Inset: strain map of the
 215 CsPbBr₃ microcrystal from which these data are taken. **f**, Calculated strain energy release rate,
 216 *G*, for channelling cracks and edge delamination. $\Gamma_0=0.24$ J/m² (polycrystalline) and $\Gamma_0=2.72$
 217 J/m² (single-crystalline) are minimum and maximum cohesive fracture energies for MAPbI₃,
 218 respectively. Figures adapted with permission from: **a**, ref.³ under a Creative Commons licence
 219 (<https://creativecommons.org/licenses/by/3.0/>); **b**, ref.⁴¹ under a Creative Commons licence
 220 (<https://creativecommons.org/licenses/by/4.0/>); **c**, ref.⁴³, American Chemical Society; **d**, ref.¹⁶
 221 under a Creative Commons licence (<https://creativecommons.org/licenses/by/4.0/>); **e**, ref.⁵,
 222 American Chemical Society; **f**, ref.¹¹, Elsevier.

223 3.1 Impact on device performance

224 The impact of strain on device performance is complicated by the apparently contrasting
225 responses of different perovskite systems to strain and the problem of defining an ‘unstrained’
226 reference state. To illustrate this, Fig. 3a shows time-resolved photoluminescence (PL) for a
227 MAPbI₃ film³, showing regions with greater local compressive strain (relative to the average
228 *d* spacing of the film) associated with the shorter PL lifetime, albeit the net strain on the film
229 is unknown. By contrast, in (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} films (Fig. 3b) the PL lifetime is
230 reported to increase upon compressive strain⁴¹. The reason for these apparent differences may
231 be complex, and one must consider how to best benchmark absolute strain and how the different
232 compositions or growth methods will impact both strain and recombination, for example, due
233 to photodoping in the mixed-component systems⁴². Further, Fig. 3c shows that the bandgap
234 increases for FA_{1-x}Cs_xPbI₃ but decreases for FA_{1-x}Cs_xSnI₃ with increasing Cs content, despite
235 a reduction in lattice parameter in both cases⁴³. These conflicting trends are attributed to
236 octahedral tilting dominating over isotropic structural contraction in FA_{1-x}Cs_xPbI₃ and highlight
237 the importance of probing the various structural degrees of freedom in the perovskite.

238 To maximise device efficiency, any nonradiative recombination must be minimised as this
239 leads to power losses. While most defects in halide perovskites are benign, there are still deep
240 trap states, which are detrimental to performance. For example, large variations of intragrain
241 crystallographic orientations and concomitant local strains are linked to higher trap densities³⁶.
242 Furthermore, larger grains exhibit more sub-grain misorientation leading to higher trap
243 densities. This suggests that managing local strain is even more critical than tuning
244 morphological grain size for minimising nonradiative recombination. At the sub-grain level,
245 twinning has been shown to be ubiquitous in FA-based systems due to the low twin formation
246 energies⁴⁴; however, these are expected to be benign from a carrier recombination perspective³⁹.

247 To understand the effects of strain on the band structure of halide perovskites we must first
248 recognise that the valence band is governed by the anti-bonding overlap between Pb *s* orbitals
249 and halide *p* orbitals, while the conduction band is dominated by the non-bonding overlap
250 between Pb *p* orbitals with minor contributions from halide *p* orbitals. Strain-induced changes
251 in Pb-X bond lengths and bond angles (Pb-X-Pb) and associated changes in orbital overlaps
252 lead to changes in band dispersion⁴⁵. In turn, the bandgap increases with increasing tensile
253 strain and decreases with increasing compressive strain⁴¹. Carrier mobility has been shown to
254 increase with increasing compressive strain due to a reduction of carrier effective mass, though
255 at higher magnitudes of compressive strain the mobility decreases due to generation of
256 dislocations⁴. In 2D A₂PbBr₄ [(A= *n*-butylammonium, *n*-octylammonium, or
257 phenethylammonium (PEA)]⁴⁶, mobility was increased by tuning the cation stacking pattern,
258 alleviating microstrain, and reducing electron-phonon interactions. Few-layer 2D perovskites
259 are also observed to exhibit an expanded structure accompanied by a blue-shifted PL emission
260 peak in comparison to bulk 2D perovskites⁴⁷. These reports show that strain is a key
261 optimisation parameter and an essential structural lever for modulating device performance.

262 **3.2 Impact on device stability**

263 Intrinsic device stability is arguably the most important topic for halide perovskites. Ion
264 migration has been associated with device instability, owing to degradation caused by atomic

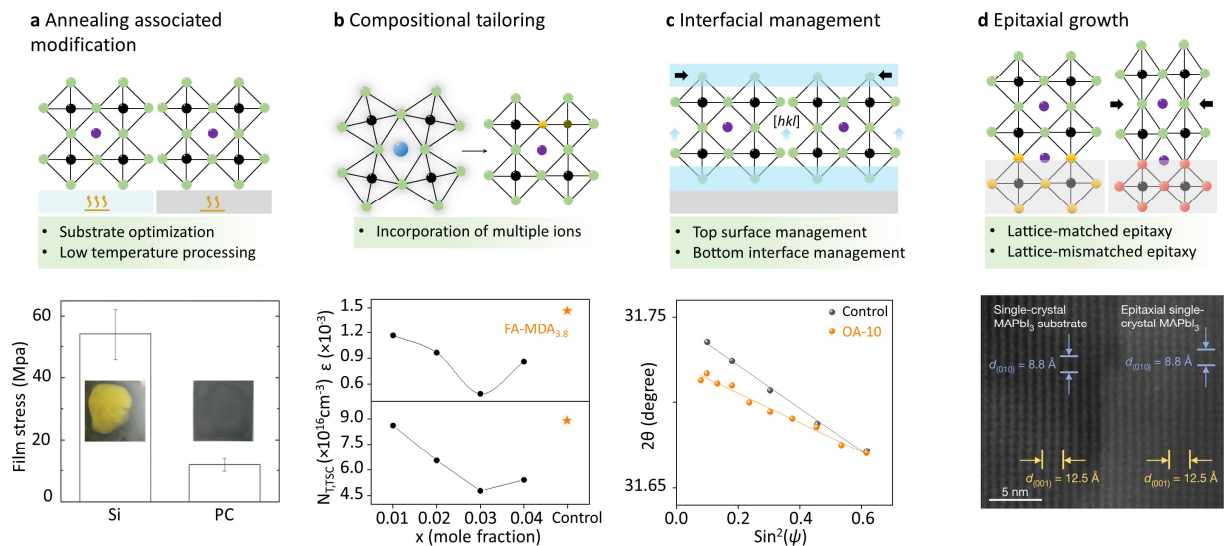
265 rearrangement or redox chemistry between migrated ions and other species. Evidence suggests
266 that the halides are the most mobile ions in halide perovskites^{48, 49}. The activation energy of
267 ion migration has been reported to increase with compressive strain and decrease with tensile
268 strain (Fig. 3d)¹⁶. This result is consistent with other reports of temperature-dependent
269 conductivity measurements, where increasing compressive strain (relieving tensile strain)
270 results in more stable films¹⁷. However, here substrates were generally bent along only one
271 axis and so the stress applied was uniaxial. Due to Poisson's effect, there will be strains of
272 opposite signs in the directions perpendicular to the direction of the uniaxial strain. As such,
273 both tensile and compressive strains are expected to exist along different directions in the plane
274 of the film. Furthermore, consideration of the impact of cracks and wrinkles in the film will be
275 needed, as these features may be induced in such bending studies and will affect ion migration.
276 The increasing compressive strain has also been shown to increase the radiation hardness of
277 CsPbBr₃ microcrystals (Fig. 3e)⁵. Further, it has been reported that increasing hydrostatic
278 pressure increases the range of miscible I:Br ratios in MAPb(I_{1-x}Br_x)₃, and inhibits ion-
279 migration-driven halide segregation⁵⁰. There is still much to be understood about the
280 fundamental mechanisms of halide segregation. Future work will need to explore, for example,
281 how the material's elastic energy changes to maintain the coherency of the underlying lattice
282 in mixed component systems with different ionic sizes⁵¹⁻⁵³. The variation of the free energy as
283 a function of composition in alloyed perovskite systems due to coherency strains may, in turn,
284 dictate the miscibility gap of the mixed ions, and elucidate the specific segregation
285 mechanisms⁵⁴.

286 Strain also affects the stability of halide perovskites by regulating the thermodynamics of defect
287 generation. Density functional theory (DFT) calculations show that the defect formation energy
288 of the halide vacancies in halide perovskites decreases with increasing tensile strain¹⁶. The
289 defect concentration in tensile strained (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} is reported to be higher than
290 that in its less strained counterpart (2.6×10^{16} versus 2.1×10^{16} cm⁻³)⁵⁵. Moreover, calculations
291 show that shallow defect states in MAPbI₃ close to the valence band become even shallower
292 under low hydrostatic pressure (0.3 GPa)⁵⁶. However, in FAPbI₃ and FA_{0.75}CS_{0.25}PbI₃, a higher
293 pressure (2 GPa)⁴⁵ has been reported to transform shallow iodide vacancy defects into deep
294 level states. More critical comparisons on identical perovskite systems will be needed to
295 generalize such observations. Other computational work suggests that under biaxial strain
296 (compressive or tensile), the lowest energy phase of MAPbI₃ is orthorhombic, indicating the
297 presence of a thermodynamic driving force for a phase transition from the desired cubic phase⁵⁷.
298 This contrasts with work on the FA-based analogue showing that compressive strain suppresses
299 the transition from the cubic to tetragonal phase⁴. This is another example of nominally similar
300 halide perovskite systems responding to strain in opposing ways. Similar phase retention
301 behaviour is observed in MAPbI₃ films where the tetragonal to orthorhombic phase transition
302 is suppressed for smaller grains^{58, 59} which are speculated to be more strained than larger grains,
303 but such strain fields are yet to be directly characterised.

304 Halide perovskites must also be mechanically robust for photovoltaic applications. Grain
305 boundaries and film edges are sites of abrupt changes in film morphology and structure, and
306 therefore, are regions where stress may be concentrated⁶⁰. Upon loading, a mechanical fracture

307 can propagate along these boundaries and edges when stress overwhelms the energetic
 308 threshold of film fracture. For a given stress value and film thickness, the propensity to crack
 309 and delaminate can be calculated through their respective strain energy release rates, G , which
 310 scales according to $G \propto \frac{\sigma^2 h}{E}$, where σ is the stress, E is the Young's modulus, and h is the
 311 layer thickness⁶⁰. If G exceeds the cohesive fracture energy, Γ_0 , (an index reflecting the
 312 resistance to mechanical fracture), film cracking and/or delamination will occur. Γ_0 for halide
 313 perovskites falls below 1.5 J/m^2 , making these materials mechanically vulnerable to fracture⁶¹.
 314 Furthermore, film cracking is more energetically favourable than film delamination (Fig. 3f)¹¹.
 315 An aim of the field should be to obtain absorber layers with higher Γ_0 ($>10 \text{ J/m}^2$)⁶¹ to improve
 316 mechanical robustness, with this being even more pertinent for flexible devices⁶². Any residual
 317 stresses in perovskites, or adjacent device layers, require careful consideration to minimise the
 318 potential of fracturing.

319 4. Strain engineering to mitigate adverse effects



320

321 **Fig. 4| Strain engineering in halide perovskite photovoltaics.** **a**, Annealing associated
 322 modification: Top, diagram of how to prevent annealing associated strain generation. Bottom,
 323 measured stress for MAPbI₃ formed on silicon (Si) and polycarbonate (PC) at 100 °C. Insets
 324 show photographs of perovskites deposited on both substrates after 45 h of dry heat aging
 325 (85 °C and 25% relative humidity). The perovskite degrades to the yellow phase only on the Si
 326 substrate where there is greater thermal expansion mismatch. **b**, Compositional tailoring: Top,
 327 illustration of the incorporation of multiple ions. Bottom, microstrain calculated in samples
 328 consisting of fluorine-doped tin oxide (FTO)/mesoporous TiO₂/(FAPbI₃)_{1-x}(MC)_x (upper plot)
 329 and trap density (lower plot) where MC is a mixture of MDA²⁺ and Cs⁺ with the equimolar
 330 amount and the orange star indicates control perovskite [(FAPbI₃)_{0.972}(MDACl₂)_{0.028}], $N_{T, TSC}$
 331 is the trap density. **c**, Interfacial management: Top, illustration of perovskite interface
 332 management. Bottom, linear fit of 2θ vs. $\sin^2 \psi$ for n-octylammonium modified (OA-10) and
 333 control perovskite films. A reduced slope represents a reduction of tensile stress in perovskite

334 films. **d**, Epitaxial growth: Top, illustration of epitaxial growth. Bottom, a high-resolution
335 transmission electron microscope image showing the interfacial area of the epitaxial single-
336 crystal MAPbI₃ on a MAPbI₃ substrate. Figures adapted with permission from: **a**, ref.²⁰, Wiley-
337 VCH (bottom); **b**, ref.¹, AAAS (bottom); **c**, ref.⁵⁵, Wiley-VCH (bottom); **d**, ref.⁷⁶, Springer
338 Nature Ltd (bottom).

339 **4.1 Annealing associated modification**

340 Thermal annealing is a routine step in the preparation of polycrystalline perovskites. However,
341 any thermal expansion mismatch between the perovskite thin film and adjacent layers must be
342 considered for strain generation in perovskites and ideally minimised. The bottom panel in Fig.
343 4a shows aged MAPbI₃ films, one on a Si substrate that has degraded to a yellow colour (PbI₂),
344 and the other on a polycarbonate substrate that remains as a dark absorbing film. The difference
345 is attributed to the larger in-plane tensile strain in the film on Si due to the greater CTE
346 mismatch between the perovskite and Si substrate²⁰. One way to address this issue is through
347 modification of the annealing process. A variation on standard film fabrication procedures is
348 where the perovskite film is fully formed on the substrate at room temperature (with or without
349 post-annealing) thereby lowering the tensile strain in the film²⁰. Another low-temperature
350 approach has enabled photovoltaic devices to deliver an impressive PCE of 23.1% by utilising
351 amine assisted crystallization at room temperature⁶³. While these reports show the potential for
352 annealing associated modification of the deposition process, further innovation is required to
353 avoid large residual strains in films. Comparing solution-processed films with thermally
354 evaporated ones (in which the photoactive black perovskite phase can form even without
355 annealing⁶⁴) may also provide insights into any hidden role played by solvent molecules⁶⁵.
356 Further, a vertical temperature gradient through the device stack is present during annealing
357 which can set up chemical and strain gradients along this direction⁴¹. However, such features
358 are difficult to characterise without depth-dependent and multi-dimensional techniques.

359 **4.2 Compositional tailoring**

360 Compositional tailoring (Fig. 4b) involves substituting different ions into lattice sites and has
361 been reported to be effective in reducing microstrain in halide perovskites. For example, the
362 incorporation of ions with radii smaller than FA (253 pm)⁶⁶, such as MA (217 pm)⁶⁶ and Cs
363 (167 pm)⁶⁶ at the A-site^{2, 22}, and/or Br (196 pm)² and Cl (181 pm)² at the X-site^{2, 22}, has been
364 proposed to reduce the microstrain in FAPbI₃-based systems, with a potential strain relaxation
365 mechanism where these additives could decrease the B-X bond lengths and the B-X-B bond
366 angles², a conclusion ascertained from DFT calculations². Another approach is to incorporate
367 larger cations (such as PEA) to form 2D or 2D/3D perovskites. This has been shown to promote
368 preferred crystal orientation, reduce Bragg peak width, and increase Bragg peak area (generally
369 indicative of reduced microstrain), yielding improved device efficiency over the 3D-only
370 controls⁶⁷. Recently, simultaneous incorporation of smaller Cs and larger MDA
371 (methylenediammonium; 262 pm) A-site cations into FAPbI₃ has been shown to suppress
372 microstrain without increasing the bandgap¹. The reported microstrain relaxation was
373 associated with a decrease in defect concentration (Fig. 4b, bottom) and nonradiative
374 recombination losses, leading to a PCE of ~24.4% and promising stability¹. In this work, the

375 authors note that the simultaneous introduction of larger and smaller ions could modify the
376 local strain in the perovskite lattice, yet the octahedral tilting they proposed, as a mechanism
377 for such microstrain reduction still requires direct experimental evidence. Determination of
378 local atomic structure, for example with pair distribution function analysis, high-resolution
379 electron diffraction, or X-ray fine structure measurements, will be of great value to confirm or
380 refute proposed strain relaxation mechanisms.

381 Compositional tailoring has achieved success in enhancing device performance but commonly
382 used compositions employing multiple A-site cations (FA/MA or Cs/FA/MA) can be
383 detrimental to the mechanical stability of films⁶⁸. We note that current ubiquitous spin coating
384 procedures including antisolvent quenching can result in smaller grain sizes, which is
385 correlated with a greater susceptibility to film fracture⁶⁸, accompanied by reduced cohesive
386 fracture energy, Γ_0 . The common practice of using a slight excess of PbI₂ in precursor solutions
387 to achieve higher performances⁶⁹ can also reduce film stability⁶⁸, in addition to any photo-
388 instabilities it introduces⁶⁹. By contrast, additive species such as 1,2-diaminopropane and
389 butylphosphonic acid 4-ammonium chloride can be added to precursor solutions to crosslink
390 between perovskite grains^{61,70}, thereby reducing the film's propensity to mechanically fracture.

391 **4.3 Interfacial management**

392 It is of interest to examine if strain can be modified by inserting an interlayer between the
393 perovskite and the substrate. To date, some compliant interlayers have been reported to relax
394 strain in perovskites caused by CTE mismatch between substrate and perovskite^{40,71}. However,
395 given the thickness of typical interlayers (roughly a few tens of nanometers), the underlying
396 mechanisms are likely to be more complex. For example, the use of a compliant
397 polytriarylamine interlayer on top of a Si substrate, with a thickness of ~20 nm, will not have
398 a significant effect on alleviating the CTE-mismatch-induced strain experienced by the top
399 perovskite layers²⁰. Furthermore, despite claims in recent reports^{18,72}, interlayers are unlikely
400 to facilitate strain control by minimising the lattice mismatch at the interface because the
401 perovskite growth processes are unlikely to be epitaxial⁷³ (owing to the typical solution
402 processing methods of these films) and thus lattice matching with the substrate may, in general,
403 not be relevant. In other work, it has been proposed that the top contact layer can be modified
404 for use as a strain compensation layer. For example, poly[5,5-bis(2-butyloctyl)-(2,2-
405 bithiophene)-4,4'-dicarboxylate-alt-5,5'-2,2'-bithiophene], which has a larger CTE than
406 CsPbI₂Br, could lead to a compressive strain on the CsPbI₂Br layer below, offsetting the
407 residual tensile strain in the perovskite¹⁶. Constructing a 2D perovskite layer on top of the 3D
408 perovskite has also been shown to reduce the residual stress in perovskites (Fig. 4c, bottom)⁵⁵,
409 based on 2D perovskites exhibiting a lower Young's modulus. However, care must be taken to
410 determine whether the corresponding stress and strain reductions in perovskites are truly due
411 to the mechanical action of these contact layers. Furthermore, efforts should be made to assess
412 the stress and strain evolution at the 2D/3D interface, which is likely to be influenced by the
413 orientation of the 2D perovskites relative to their 3D counterpart⁷⁴. Besides, not all 2D/3D
414 interfaces will be sufficiently stable without further management: for instance, it has been

415 proposed that invasive ions from the underlying 3D perovskites interrupt the Van der Waals
416 interactions in the 2D layered perovskites⁷⁵, which could drive layer slippage and even fracture.

417 Epitaxy is a well-established material growth technique for introducing controlled levels of
418 strain into materials by judiciously choosing lattice-matched/mismatched substrates. Recently,
419 successful epitaxial growth of α -FAPbI₃ was achieved by tailoring the composition of a
420 MAPbCl_xBr_{3-x} single-crystal substrate⁴. Further compositional tuning also allowed various
421 levels of strain to be imparted onto the α -FAPbI₃ epilayer, with low levels of compressive strain
422 found to notably enhance the phase stability. In other work, solution-phase epitaxial growth of
423 MAPbI₃ was enabled by using lattice-matched MAPbI₃ substrates (Fig. 4d, bottom), with an
424 impressively large area (>25 cm²) and the absence of dislocations⁷⁶. Heteroepitaxial growth of
425 halide perovskites directly on top of charge transport layers could be useful, but this will further
426 necessitate expanding the current library of contact layers for halide perovskite devices.
427 Another interesting aspect of epitaxial growth is the tendency of phase impurities to epitaxially
428 grow alongside perovskite phases⁷⁷. Given the critical need to minimise phase impurities,
429 especially those harmful to performance and stability, further research is needed to understand
430 the role of epitaxial growth in stabilising halide perovskites. Nonetheless, epitaxial techniques
431 are comparatively expensive and their use risks negating this key advantage of halide
432 perovskites (that of inexpensive and scalable processability) in the face of more efficient and
433 stable III-V or Si-based equivalents.

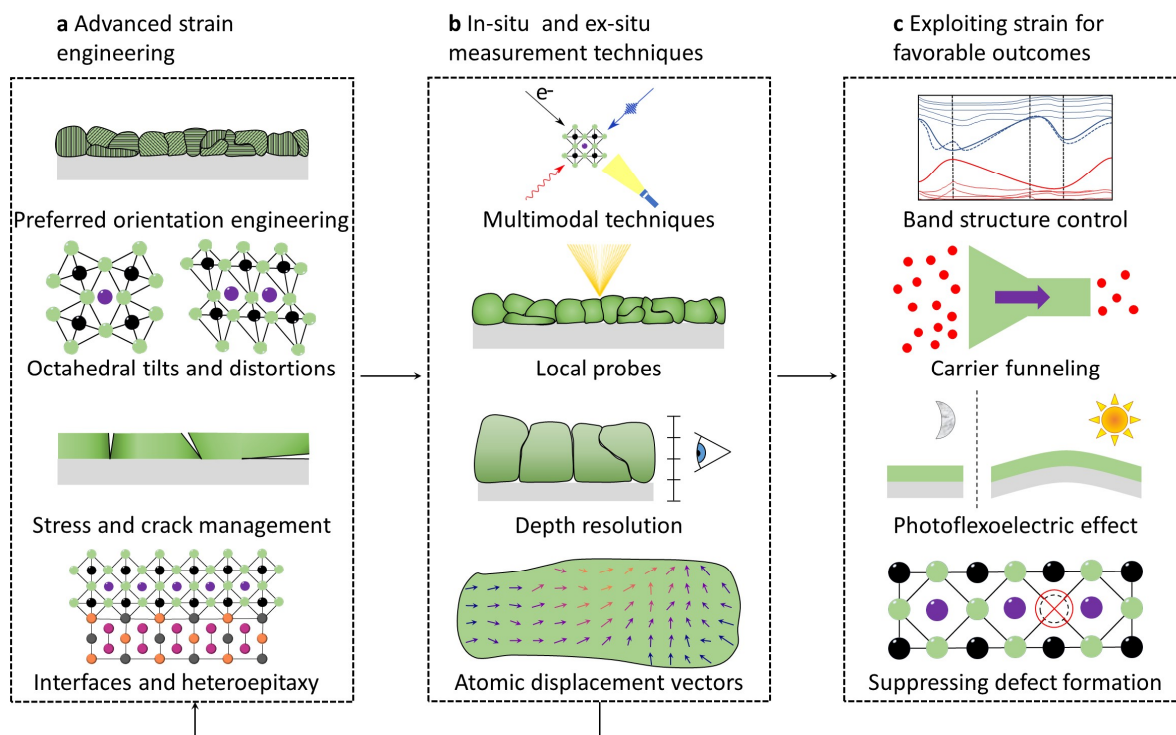
434 In addition, it has been reported that some contact layers in perovskite photovoltaics suffer
435 intrinsic fragility⁷⁸ or inadequate adhesion to the perovskites⁷⁹⁻⁸¹, and perovskite photovoltaics
436 with these undesirable characteristics will have reduced stress tolerance and mechanical
437 integrity. Approaches to address this issue have been proposed, including the design of
438 materials in which strong covalent bonds can form after deposition from the solution state⁷⁸,
439 the use of self-assembled interlayers⁷⁹, low-dimensional perovskite capping layers on top of
440 3D perovskites⁸⁰, and graded interfaces⁸¹. Such approaches will be critical for increasing the
441 film's cohesive fracture energy, Γ_0 , and ensuring mechanical integrity of the operating
442 devices⁷⁹.

443 **5. Challenges and Outlook**

444 To tackle the many outstanding questions about the links between strain and material properties
445 in perovskite photovoltaics, we propose an iterative workflow whereby strain is tuned with
446 advanced strain engineering (Fig. 5a), and more fully characterised using powerful in situ and
447 ex situ measurement techniques (Fig. 5b) with the knowledge fed back to improve strain
448 engineering approaches. Finally, the result (Fig. 5c) will be the ability to not only suppress the
449 adverse effects of strain but also to exploit strain for favourable outcomes in devices.

450

451



452

453 **Fig. 5| Workflow for unlocking the potential of strain in perovskite devices.** **a**, Strain can
 454 be applied systematically to halide perovskites with advanced strain engineering. **b**, Cutting-
 455 edge in- and ex-situ characterisation techniques are employed to fully characterise strain in
 456 halide perovskite samples. **c**, Strain is exploited to realise better devices.

457 5. 1 Advanced strain engineering

458 The association of nonradiative losses with orientation mismatch³⁶ suggests that engineering
 459 films with greater preferred orientation should be targeted for improved optoelectronic
 460 properties. Further, one may be able to channel strain into crystallographic directions where
 461 the presence of strain is less detrimental. For example, microstrain in FAPbI₃ in the $\langle 111 \rangle$
 462 direction, in particular, is associated with reduced film stability²². Meanwhile, Young's
 463 modulus exhibits a directional anisotropy, with $E_{110} < E_{100}$, in cubic MAPbX₃ (X=Br, Cl),
 464 making it more facile for deformations to propagate in the $\langle 110 \rangle$ direction than in the $\langle 100 \rangle$
 465 direction⁸². However, care must be taken when extracting microstrain values for particular
 466 crystallographic directions from individual Bragg peaks, especially if assuming negligible
 467 crystallite size broadening based on the morphological grain size given the presence of sub-
 468 grain heterogeneities¹³.

469 Tilting of the octahedral BX₆⁴⁻ units has been well studied in other systems based on the
 470 perovskite structure⁸³ and octahedral distortions including cation off-centring are also known
 471 in halide perovskites. However, study of octahedral tilting and distortion in halide perovskites
 472 are often limited to Goldschmidt tolerance factor considerations, which leads to difficulties
 473 when considering molecular cations that can form hydrogen bonds⁸³. Although some
 474 researchers have noted the link between octahedral tilting/distortion and strain⁸⁴, explicit

475 characterisations of such structural features will be critical given the relationship between
476 important properties such as bandgap and the largest metal-halide-metal bond angle⁸⁵.

477 The determination of stress and its impact on halide perovskites are under-explored areas and
478 merit more dedicated studies. Uncompensated stress can cause fracturing of the perovskite
479 leading to the loss of Ohmic contacts with the charge-selective layers and allowing the ingress
480 of detrimental moisture and oxygen⁸⁶. Stress analyses could explain film wrinkling, a common
481 mechanism by which a film can relieve stress during formation⁸⁷. Additionally, from a
482 thermodynamic perspective, spatially heterogeneous distributions of stress can result in the
483 local accumulation of elastic energy in films which is relevant given ions will rearrange until
484 their diffusion potentials are uniform across the film⁵¹. Stresses will occur on both short and
485 long length scales, with delamination⁶⁰ and cracking⁸⁸ being problems at the scale of tens of
486 micrometres, and emergent microstresses at the grain boundaries and other operational stresses
487 being concerns on the nano to atomic scale^{11, 89}. Defect pooling at grain interfaces can reduce
488 the material's mechanical integrity by causing these interfaces to serve as fracture points⁶¹.
489 Given the presence of sub-grain features and misorientations, solving the above issues will
490 likely require strategies beyond just tuning processing methods. Stress can either be determined
491 directly through curvature measurements^{20, 35, 87}, or calculated indirectly, via interrogation of
492 strain ascertained through material structure studies with use of appropriate proportionality
493 constants. However, such indirect calculations of stress come with many complexities^{88, 90}. A
494 common method for the measurement of the in-plane residual stresses in films is the $\sin^2 \psi$
495 method^{88, 90}.

496 Beyond the perovskite bulk, regulating harmful strain at the substrate/perovskite interface is
497 also crucial for improving device performance. Substrates with aligned nanopores have been
498 employed to confine crystallization and impose compressive strain on perovskites, with the
499 strain level dependent on the pore size⁹¹. Similar results are achieved through the manufacture
500 of textured perovskite films⁹². Furthermore, perovskites that are infiltrated into a porous
501 $\text{TiO}_2/\text{ZrO}_2/\text{Carbon}$ layer have been shown to exhibit improved mechanical integrity⁶⁸. Another
502 emerging approach to reduce strain is to apply 2D materials (such as transition metal
503 dichalcogenides) as interlayers where the Van der Waals interaction enables perovskites to
504 expand/contract freely during heating/cooling processes⁹³. We note, however, the key
505 challenge of synthesising such 2D materials without dangling bonds. Regulating strain may
506 also involve management of lattice matching at semiconductor interfaces, but this approach
507 has received limited attention to date, probably for two reasons: first, there is a debate about
508 whether typical solution processing of perovskites involves epitaxial growth processes, and
509 second, the perovskite structure is sufficiently accommodating that device efficiencies have
510 not suffered appreciably in the face of poorly lattice-matched interfaces. However, it is possible
511 that some more sinister ramifications of poor lattice matching, such as delamination of layers
512 in the device stack, only become evident after stringent, long-term operational testing⁶¹.
513 Looking towards conventional semiconductors, epitaxial growth of perovskites on hetero-
514 substrates can allow control of strain at the interface by tuning lattice matching. A halide
515 perovskite epilayer grown on functional layers, without secondary transfer of the epitaxial
516 perovskite, could be desirable for high-performance photovoltaic applications, and there is a

517 wealth of literature on other materials with domain matching epitaxy⁹⁴. Additionally, the
518 application of intervening layers allows high-quality epitaxial growth of semiconductors with
519 strain applied through carefully chosen lattice mismatches⁶⁰.

520 The strain management methods proposed in this work will apply to a wide range of perovskite-
521 based photovoltaics including Sn- and Sn-Pb based devices^{95, 96} and tandem cells⁹⁷. Effective
522 strain management will also be critical when employing perovskites on flexible substrates or
523 upscaling to full-sized modules⁶⁸. Additionally, daily or seasonal temperature, spectral, and
524 light intensity changes present important challenges for both stress and strain management in
525 operating devices.

526 **5.2 In and ex situ measurement techniques**

527 Multimodal correlative microscopy can provide deep insights into the underlying physics in
528 halide perovskites. For example, correlation of strain fields with photoluminescence,
529 compositional, and time-resolved data sets will uncover new links between strain and material
530 performance^{3, 36}. Integrating tight environmental control (of light, heat, humidity, UV exposure,
531 etc.) and sample encapsulation with these measurement techniques will allow assessment of
532 the evolution of strain in operating devices.

533 The presence of spatially heterogeneous strain in halide perovskite samples necessitates the use
534 of local probes for studying strain. Current state-of-the-art film compositions contain many
535 components which are known to segregate^{98, 99}. To adequately assess the impacts of this
536 segregation, a local approach to strain characterisation is required, further employing
537 techniques such as scanning probe nano-XRD and X-ray fluorescence¹⁰⁰. There is also
538 evidence for rich chemical heterogeneity at the grain and sub-grain length scales¹³.

539
540 In alloyed systems⁶⁶, including the Pb/Sn and mixed cation and halide systems, it is still unclear
541 how the alloyed components are arranged – whether they vary from unit cell to unit cell, or if
542 they tend to form clusters across the sample¹⁰¹. In the case of mixed halide samples, given the
543 evidence for inhomogeneous halide distributions⁴², the observed compressive/tensile “strain”
544 may be due to changes in composition rather than stress. The community, therefore, needs to
545 expand its understanding of local chemical distributions through the use of nanoscale chemical
546 mapping techniques^{102, 103}. Further, ion re-distribution in perovskites can gradually occur in
547 response to strain, which, in turn, varies the strain distribution in perovskites¹⁶. To overcome
548 these challenges, in-situ strain detection is required to view strain propagation in real-time.

549 Strain measurements to date have predominantly focused on the in-plane direction, and further
550 work to simultaneously monitor out-of-plane strain is of interest. Furthermore, the relative
551 importance of strain in the perovskite bulk and strain at the perovskite surface is currently
552 unknown. A greater focus on depth-resolved techniques such as grazing incidence X-ray
553 scattering will be required.

554 Most reports on strain to date have been on neat film samples as opposed to device stacks, and
555 so these works miss the complex interactions of the perovskite with adjacent layers in the

556 device. Local heterogeneities in the perovskite material may also exist due to the influence of
557 other device layers. Under electrical bias, there is evidence for photostrictive effects along with
558 ion migration⁴⁸, the activation energy of which can be altered by strain and is a vitally important
559 phenomenon to understand in the field. Thus, developing techniques for in operando
560 characterisations of microstrain in full and half devices for a complete understanding of the
561 impact of strain will be fruitful.

562 Advanced coherent diffraction imaging techniques such as Bragg coherent diffraction imaging
563 and Bragg ptychography can potentially allow reconstruction of full three-dimensional maps
564 of atomic displacement vectors¹⁰⁴. Resolving atomic displacement vectors would allow one to
565 uncover strain fields in halide perovskites that may be characteristic of certain crystal
566 aberrations, facilitating “defect diagnosis”¹⁴. Correlation of these strain fields with other
567 optoelectronic data would yield rich insights and should be a future research focus. Atomic
568 displacement vectors can also be resolved with cryogenic and high-resolution transmission
569 electron microscopy measurements^{77, 105}. However, attention must be paid to the beam dose in
570 these measurements, which might introduce undesirable defects and/or lead to material
571 decomposition if not performed carefully^{106, 107}.

572 **5.3 Exploiting strain for favourable outcomes**

573 There is a wealth of literature on using strain in other material systems to enhance material
574 characteristics by modulating band structures¹⁰⁸, electrical conductivities¹⁰⁹, electron-phonon
575 coupling and ion migration¹¹⁰, among other properties¹¹¹. Modulating strain could see several
576 exotic effects realised in halide perovskites leading to new device use-cases. First-principles
577 computational work suggests polar phases in lead-iodide perovskites may be realisable with
578 large Rashba splitting at room temperature via tensile strain¹¹². Being able to control Rashba
579 splitting provides an additional lever for tuning carrier dynamics¹¹³. Distinct chemical domains
580 with distinct bandgaps within mixed-component films may allow for carrier funnelling and
581 devices based on such effects^{3, 41, 114}. Strain gradients have also been utilised in halide
582 perovskites to enhance flexoelectric responses with corresponding photoflexoelectric effects
583 demonstrated in MAPbI₃ single crystals¹¹⁵. While engineering such exotic effects into real-
584 world devices is yet to be realised, these reports show that strain plays a critical role in the
585 electronic structure of halide perovskites, and that it can indeed be exploited. Strain
586 management can lead to better material quality by suppressing the formation of defects due to
587 ion migration in the material.

588 A robust understanding of the origins and effects of strain in halide perovskite-based devices
589 is needed to facilitate future breakthroughs. This will be especially critical in the construction
590 of perovskite/Si and perovskite/perovskite tandems, where many layers may each contribute
591 both stress and strain components, influencing overall efficiency and stability. As the halide
592 perovskite community continues to push the envelope on long-term operational stability, strain
593 will be a key parameter for optimisation and a versatile lever for control in more exotic devices.

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606 **Author contributions**

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609 **Competing interests**

610 S.D.S. is a co-founder of Swift Solar, Inc. All other authors declare no competing interest.

611 **Additional information**

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