

Compositional Heterogeneity in $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ Perovskite Films and its Impact on Phase Behavior

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Abstract

Hybrid organic inorganic lead halide perovskite semiconductors of the form $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ are promising candidate materials for high-efficiency photovoltaics. Notably, cation and anion substitution can be used to tune the band gaps to optimize performance and improve stability. However, multi-component materials can be prone to compositional and structural inhomogeneity and the extent, length scale and impact of this heterogeneity on lead halide perovskite properties is not well understood. Here we use synchrotron X-ray diffraction to probe the evolution of crystal structure across the tetragonal-to-cubic phase transition for a series of $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ thin films with $x = 0.05$ to 0.3 and $y = 0.17$ to 0.40 . We find that the transition occurs across a broad temperature range of approximately 40°C , much larger than for pure compounds such as MAPbI_3 and MAPbBr_3 . We hypothesize that this smearing of the phase transition is due to compositional inhomogeneities that give rise to a distribution of local transition temperatures and we estimate the composition varies by about 10 % to 15 % with likely greater heterogeneity for the halide anion than the cation. This approach of mapping the transition is a simple and effective method of assessing heterogeneity, enabling evaluation of its impact.

Broader context

This paper focuses on metal halide perovskite thin films, a system of wide interest for photovoltaic applications. Particularly, perovskite films of the form $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ have sparked a lot of enthusiasm for use in tandem solar cell applications since their bandgap is particularly well suited to complement Si. However, these alloyed materials are potentially inhomogeneous, which have implications on the materials properties, including the propensity to photo-induced instability and phase demixing. Stability is one of the most significant challenges faced in these materials before commercialization of solar cell devices. Despite extensive studies, the nature of the inhomogeneities

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25 and the extent of compositional heterogeneity is still not well understood, as there are few simple
26 methods to assess this. It is essential to quantify heterogeneity, particularly at the nanoscale, to
27 understand its impact. Understanding the complex phase behavior is of paramount importance
28 as the phase transitions are around operational temperature of solar devices.

29 Introduction

30 Over the last decade, hybrid organic inorganic metal halide perovskites (MHPs) have sparked tremen-
31 dous enthusiasm due to their favorable optoelectronic properties [1, 2] for applications in both single
32 junction and tandem solar cells as well as other optoelectronic devices [3, 4, 5]. Perovskites have the
33 general chemical formula ABX_3 where for MHPs, A is a monovalent cation, B is a divalent cation,
34 and X is a halide anion. The unit cell comprises corner-sharing BX_6 octahedra that form a cubo-
35 octahedral cavity filled by the A-site cation. The perovskite crystal structure accommodates a wide
36 compositional space, and in state-of-the-art MHP photovoltaics, A is typically a mixture of formami-
37 dinium ($FA = CH(NH_2)_2^+$), methylammonium ($MA = CH_3NH_3^+$), and Cs^+ , B is typically Pb^{2+} , and
38 X is typically a mixture of I^- and Br^- . Compositional tuning on both the A- and X-site alters the
39 material's band gap, and compositions of the form $Cs_yFA_{1-y}Pb(Br_xI_{1-x})_3$ with $0 < x < 1$ and $0.1 <$
40 $y < 0.3$ have been found to be particularly well-suited for applications as the top-cell material in
41 tandem perovskite-silicon photovoltaics [6].

42 Despite the impressive performance of MHP based solar cells, with record efficiencies exceeding
43 25% and 29% for perovskite and perovskite/Si monolithic tandem devices, respectively [7, 8], there
44 is space for improvement in several aspects before commercialization and widespread deployment
45 becomes feasible [9, 10, 11]. While state-of-the-art MHP solar cells have short circuit current den-
46 sities that are near theoretical and practical maxima, the open circuit voltage and fill factor can
47 be improved, which could be achieved by suppressing charge carrier recombination in the bulk film
48 and at interfaces. In addition, high-performing multi-cation, multi-halide MHP devices need to be
49 controllably synthesized by cost-efficient and scalable methods. While there is some debate about
50 possible limitations imposed by the toxicity of Pb^{2+} , developing high performing Pb-free solar cells
51 is desirable. Finally, convincingly demonstrating long-term stability remains a key issue [12].

52 Of these challenges, stability is, arguably, the most important. While thermodynamic stability
53 and chemical decomposition are important, photo-induced instability (or demixing) are a significant
54 challenge for multi-cation, multi-halide MHPs that have wide band gaps needed for tandem pho-

55 toovoltaics. Here illumination induces a nanoscale compositional segregation into I-rich and Br-rich
56 domains [13, 14, 15, 16]. This process requires fast halide anion diffusion that is likely facilitated
57 by high vacancy concentrations [17, 18, 19]. There is some evidence for photoinduced A-site cation
58 demixing as well [20], although mixed A-site MHPs with FA and Cs show improved photo-stability
59 [21]. While the phenomenon of photo-induced phase segregation has been intensively investigated,
60 the mechanism is still under active discussion [16]. It has been suggested that for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$
61 perovskites compositions near the tetragonal-to-cubic phase boundary are more optically stable [22].
62 We have shown that MHP crystallographic phase is not the sole determinant to stability [14], and
63 it has been postulated that initial nanoscale local compositional variations serve as nuclei for the
64 formation of I-rich segregated nanoscale domains under illumination [23, 24, 25]. Furthermore, local
65 compositional fluctuations can impact charge carrier dynamics and device performance [26]. Thus,
66 it is essential to quantify compositional uniformity, particularly at the nanoscale, to understand and
67 control its impact.

68 Studies have demonstrated optoelectronic and compositional heterogeneity [27, 28, 29] in MHPs
69 across length scales, but almost all investigations have been limited to $>0.1\text{ }\mu\text{m}$ spatial scale [30].
70 For example, de Quilettes *et al.* showed that photoluminescence (PL) intensities and lifetimes varied
71 between different regions within the same film [27]. Correa-Baena *et al.* used nano-X-ray fluorescence
72 microscopy of mixed halide MHPs to map heterogeneity in I and Br composition showing μm size
73 regions of low Br content but demonstrating improvements in uniformity for some compositions [28];
74 the same method was used also by Wieghold *et al.* to show that the elemental composition is altered in
75 single grains based on the film thickness and this inhomogeneity explained differences in charge carrier
76 dynamics [26]. Szostak *et al.* mapped chemical diversity of individual regions with nano-spectroscopy
77 [29] showing that these regions have an intrinsic heterogeneity of the organic components. Gratia
78 *et al.* used ion microscopy to map halide composition in $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{Br}_{0.15}\text{I}_{0.85})_3$ films at sub-
79 100 nm and observed $\approx 50\text{ nm}$ regions devoid of Br, and interestingly, noted no evidence for such
80 compositional segregation based on peak broadening in diffraction, an apparent contradiction [31].
81 Much of the research on heterogeneity is summarized in the review by Tennyson *et al.* [30]. Despite
82 extensive work, easily and accurately quantifying and characterizing compositional heterogeneity
83 remains a significant challenge, especially for 1 to 100 nm length scales.

84 Compositional heterogeneity can have two origins: intrinsic (or thermodynamic) and extrinsic

85 (processing-induced). The first form is the thermodynamic separation of the multi-component MHP
86 into two or more distinct phases driven by minimization of the free energy. The second likely results
87 from kinetics due to the solution-processing methods used to fabricate MHP materials that may
88 lead to chemical, structural, and electronic property heterogeneity on multiple length scales [30].
89 Distinguishing these is difficult because the MHP film may be in a kinetically trapped, metastable
90 state. We make no attempt to distinguish intrinsic and extrinsic nonuniformity in this paper and we
91 refer to both as compositional heterogeneity.

92 To the best of our knowledge, there have been no investigations of the phase behavior and phase
93 diagrams for any multi-cation, multi-halide MHP. This is likely because these are very challenging due
94 to multi-dimensional phase space and the capacity for the perovskite crystal structure to accommodate
95 many different distortions [32] that can make perovskite phase diagrams quite complex. We have
96 mapped the room temperature crystal structures for $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_{x}\text{I}_{1-x})_3$ thin films with $x = 0.05$
97 to 0.3 and $y = 0.17$ to 0.40 and identified the cubic-tetragonal solvus [14]. For the simpler four
98 component MHPs, there have been a few reports on phase behavior [33, 34, 35, 20, 36]. For A-site
99 substitution, these have shown limited incorporation of Cs in pseudocubic $\text{Cs}_y\text{FA}_{1-y}\text{PbI}_3$, about $y =$
100 0.15 in the bulk powders [33], despite theoretical predictions of much higher solubility ($y = 0.7$) [20].
101 In contrast, most MHP films show a solubility up to at least $y = 0.3$ for $\text{Cs}_y\text{FA}_{1-y}\text{PbI}_3$ [37], but these
102 may be kinetically trapped. In $\text{MAPb}(\text{Br}_{x}\text{I}_{1-x})_3$, diffraction has shown a miscibility gap up to 350 K
103 with strong intergrowth of I-rich and Br-rich crystallites and observed deviations from Vegard's law
104 [35], a point we discuss later in this manuscript. In $\text{CsPb}(\text{Br}_{x}\text{I}_{1-x})_3$, a computational study [38] has
105 predicted a single phase orthorhombic solid-solution at room temperature but phase separate into
106 Br-rich tetragonal and I-rich orthorhombic phases at 50 to 75 °C.

107 The presence of compositional heterogeneity complicates the phase transition behavior in MHPs,
108 since slight variations in composition can result in a different crystallographic phase being thermo-
109 dynamically favorable and shift the temperature where structural transitions occur. Because MHPs
110 can undergo phase transitions around operational temperatures, an understanding of their complex
111 phase behavior is necessary. In this work, we explore the nature of the tetragonal-to-cubic phase
112 transition in $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_{x}\text{I}_{1-x})_3$ perovskites and how these behaviors differ from those observed
113 in pure compounds such as MAPbI_3 and MAPbBr_3 . Crystal structure and phase transitions are
114 characterized using X-ray diffraction (XRD), and the temperature dependence of the band gap is

115 determined from the external quantum efficiency (EQE) of optimized devices.

116 We track the lattice parameter and the octahedral tilt angle across the transition and use the
117 octahedral tilt angle to characterize the evolution of the crystal structure from tetragonal into cubic.
118 We find that that this transition occurs over a broad temperature range, and we also observe a change
119 in the temperature dependence of the band gap near the temperature range where the MHP structure
120 becomes cubic. The importance of this study is that we show that photovoltaic-relevant MHP films
121 can be compositionally heterogeneous at the nanoscale and we establish a simple methodology to
122 characterize this heterogeneity.

123 Results

124 We investigate a series of $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ films with $x = 0.05, 0.17, 0.2$ or 0.3 and with $y =$
125 $0.17, 0.25$ or 0.4 that have well-controlled, and nearly constant morphology. Details on the film
126 preparation are given in ref. 14 and in the Experimental Section below.

127 Structural considerations

128 First, we briefly recall structural stability considerations. The degree of distortion from the cubic
129 perovskite crystal structure and hence the tendency to form non-cubic structures can be described
130 by the Goldschmidt tolerance factor, τ_G , which has the equation:

$$\tau_G = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1)$$

131 where r_i is the ionic radius of ion i [39]. Effectively, the Goldschmidt tolerance factor captures the
132 size mismatch between the A-site cation and the cuboctahedral cavity formed by the BX_6 octahedra,
133 assuming all of the ions are hard spheres. A τ_G greater than 1 indicates that the A-site cation is too
134 large for the cuboctahedral cavity and eventually leads to the formation of a non-perovskite phase.
135 On the other hand, a τ_G less than 1 indicates that the A-site cation is too small, which causes the
136 BX_6 octahedra to tilt in order to reduce the size of the cuboctahedral cavity. Fifteen symmetrically
137 distinct tilt patterns are possible for ABX_3 perovskites depending on the size and properties of the
138 atoms comprising the material and their interactions [40].

139 These tilt patterns are codified with Glazer notation [41] and can describe cubic, tetragonal, and

140 orthorhombic perovskite crystal structures [42, 43, 44, 45, 46]. In this notation, the letters *a*, *b*, and *c*
141 indicate the magnitude of rotation about the *x*-, *y*-, and *z*-axes, respectively, in the direction indicated
142 by the superscript. A "0" superscript indicates no rotation, so the *Pm* $\bar{3}m$ cubic crystal structure is
143 denoted $a^0a^0a^0$. Successive octahedra along an axis can either rotate in the same (in-phase) or opposite
144 (out-of-phase) directions. A "+" superscript indicates in-phase rotation of equal magnitude of the
145 octahedra along the specified axis, whereas a "−" superscript indicates that successive octahedra
146 along that axis are rotated equally in magnitude but in opposite directions. Tilt patterns that result
147 in a structure with both in-phase and out-of-phase tilts that **are** equal in magnitude are termed
148 antidistorted [47, 48]. In an antidistortive phase transition from an untilted to a tilted structure,
149 the size of the unit cell increases, but centrosymmetry is preserved [47]. Tetragonal-to-cubic phase
150 transitions in metal-halide perovksites are antidistortive.

151 While the Goldschmidt tolerance factor is a good indicator for the formation of either perovskite
152 or non-perovskite phases, it cannot be used to predict the predominance of a given crystal structure
153 within the perovskite family. Bartel *et al.* [49] have developed an alternative to the conventional
154 Goldschmidt tolerance factor, and in Supplementary section 1, we discuss the ability of tolerance
155 factors from Bartel *et al.* [49] and Goldschmidt to predict crystal structure within the perovskite
156 family.

157 Figure 1a shows the XRD patterns for two different $Cs_yFA_{1-y}Pb(Br_xI_{1-x})_3$ compositions at room
158 temperature compared with $MAPbI_3$. This figure shows that $Cs_{0.17}FA_{0.83}Pb(Br_{0.4}I_{0.6})_3$ has a cubic
159 perovskite structure (untilted $a^0a^0a^0$ in Glazer notation), while $Cs_{0.4}FA_{0.6}Pb(Br_{0.17}I_{0.83})_3$ has a tetrag-
160 onal *P4/mbm* structure that arises from in-phase tilting of the PbX_6 octahedra (denoted $a^0a^0c^+$).
161 These structures are visualized in figure 1b and figure 1c, respectively. XRD data for $MAPbI_3$, which
162 has a tetragonal *I4/mcm* structure, is also shown. As previously mentioned, the PbI_6 are tilted
163 out-of-phase ($a^0a^0c^-$) as shown in figure 1d. While both of these structures are antidistorted, they
164 are crystallographically distinct. In tetragonal $Cs_yFA_{1-y}Pb(Br_xI_{1-x})_3$ perovskites, neighboring PbX_6
165 octahedra in a given (001) plane have the opposite sense of rotation, but each (001) plane is identical.
166 In $MAPbI_3$ the arrangement of PbX_6 octahedra in a given (001) plane is similar, but the sense of
167 rotation alternates between each successive plane. In addition to $MAPbI_3$, many oxide perovskites
168 also have the *I4/mcm* space group and out-of-phase tilt pattern in the tetragonal phase [51, 52, 53,
169 54]. Note that the in-phase tilt pattern is consistent with previous works on MHPs comprising either

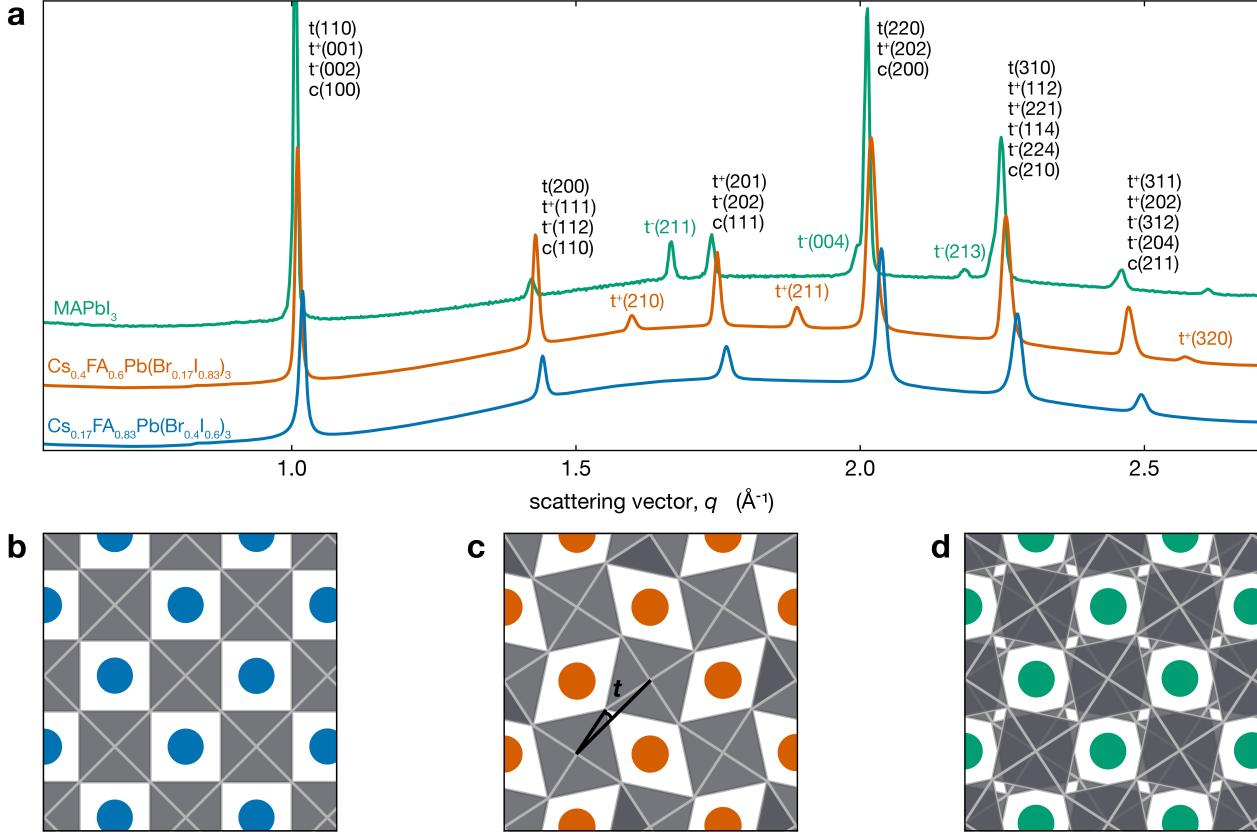


Figure 1: (a) XRD patterns for different $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ compositions exhibiting both tetragonal $a^0a^0c^+$ (tetragonal peaks indexed with t^+) and cubic $a^0a^0a^0$ structures as well as the $a^0a^0c^-$ phase of MAPbI_3 (MAPbI_3 data from Schelhas *et al.* [50]). The y-axis is linear in intensity (arbitrary units not shown) with an offset between the three patterns. Views of (b) $a^0a^0a^0$, (c) $a^0a^0c^+$, and (d) $a^0a^0c^-$ structures looking down the c-axis. Blue, orange and green spheres represent the A-site cation, and the PbX_6 octahedra are shown in grey. The tilt angle t we consider here is the angle between the black lines in (c)

170 inorganic or FA cations [55, 56, 57, 14, 58, 33, 59]

171 For $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$, the symmetry associated with in-phase tilting of the PbX_6 octa-
 172 hedra results in the emergence of several tetragonal superlattice peaks, including the $t(210)$ and $t(211)$
 173 reflections around 1.6 and 1.9\AA^{-1} , respectively, which are not observed in cubic $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$.
 174 We note that a tetragonal phase should result in the splitting of the cubic $c(100)$ peak into $t(110)$ and
 175 $t(001)$ reflections and the $c(200)$ into $t(220)$ and $t(002)$. The difference in tetragonal peak positions
 176 is expected to be about 0.5 % at room temperature. However, the observed XRD peak full width
 177 at half maximum (FWHM) for the $t(110)$ - $t(001)$ and $t(220)$ - $t(002)$ peaks is about three times larger
 178 than this expected splitting of 0.5 % and hence does not allow us to resolve two separate peaks from
 179 this measurement.

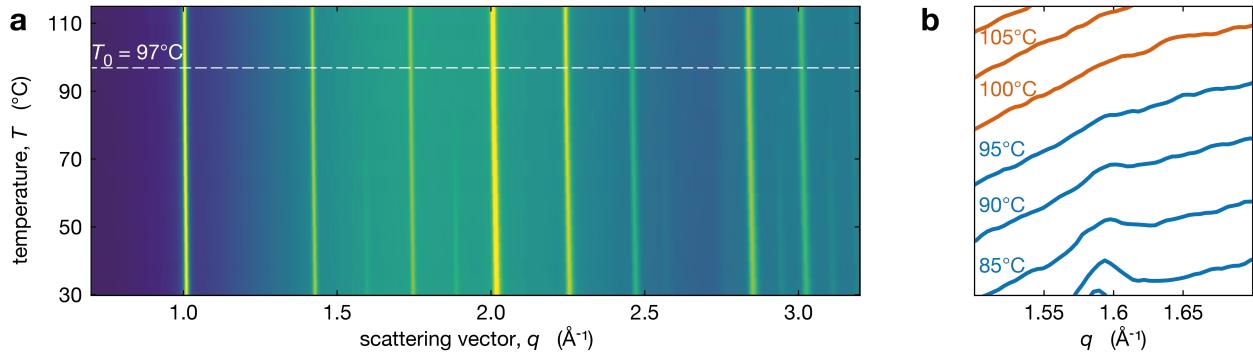


Figure 2: a) Temperature XRD map for $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ with the extracted T_0 (temperature where film is purely cubic) indicated by a dashed line. b) Evolution of the integrated intensity of the $t(210)$ superlattice peak. Temperature is increasing moving up in the vertical direction. The y-axis is linear and represents the intensity counts in arbitrary units.

180 **Phase transition monitored through the disappearance of tetragonal reflections**

181 We performed in situ XRD on the series of perovskite thin films while heating through the tetragonal-
 182 to-cubic phase transition. The temperature dependent XRD patterns in $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$
 183 are shown in figure 2a, and figure 2b shows the region near the $t(210)$ peak demonstrating the
 184 disappearance of this tetragonal superlattice peak with increasing temperature. The $t(210)$ peak is
 185 weak but observable at 95 °C, but it is not observed at 100 °C. At all temperatures, the XRD peaks
 186 have been fit with a Voigt function over a quadratic background from the substrate. Because small
 187 peaks are hard to distinguish from background and noise, we used chi-squared analysis to determine
 188 the presence of tetragonal reflection at each temperature. All calculations and fitting procedures
 189 are explained in greater detail in Supplementary section 2. We identify the temperature where the
 190 tetragonal peak intensities go to zero as T_0 . For $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ (figure 2) this is 97(3) °C
 191 (See Supplementary section 2 for details). We note that T_0 may represent a solidus temperature
 192 [14] where above T_0 , the MHP film is in a fully cubic crystal structure but below this, there exist
 193 tetragonal domains.

194 **Behaviour of the phase transition**

195 To track the phase transition behavior of $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ perovskite films, we extract the
 196 average octahedral tilt angle t from the tetragonal reflection intensities in our XRD measurements
 197 (see Supplementary section 3). Note that we define the tilt angle for one PbX_6 octahedron, with

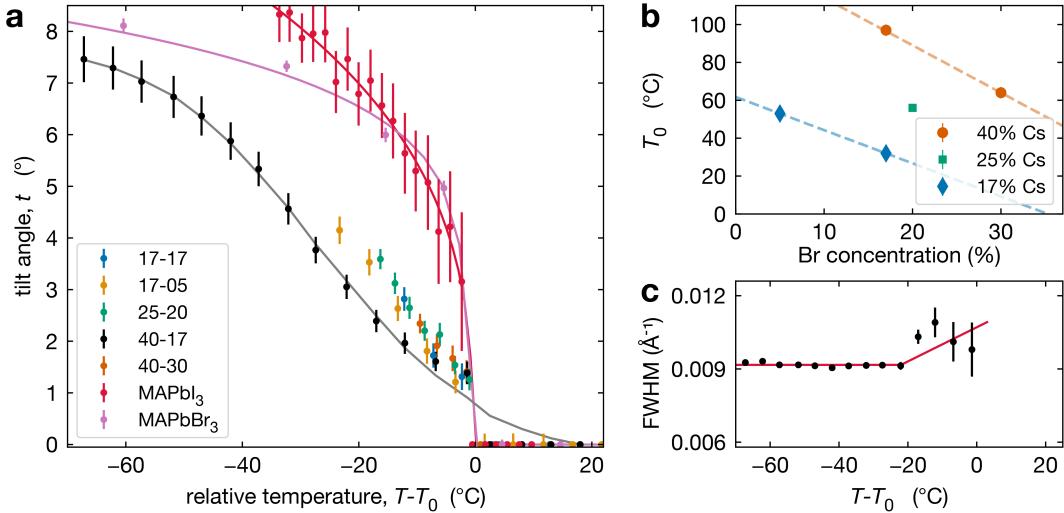


Figure 3: a) Octahedral tilt angle (symbols) plotted as a function of temperature for all compositions studied with data for MAPbI₃ thin films extracted from Schelhas *et al.* [50] and MAPbBr₃ single crystals. The solid lines show fits to these data as explained in the text. b) Temperature T_0 as a function of Br concentration at constant Cs compositions: 17% (blue diamonds), 25% (green square), 40% (red dots). c) The FWHM of the $t(210)$ peak in $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ increases slightly around 20 °C below T_0 .

198 Pb taken as the center, and the angle is relative to the cubic phase atomic position of the halide
 199 (see figure 1c). This is the tilt angle *averaged* over space and time. Hence, if the MHP film is
 200 heterogeneous, either because of extrinsic compositional variations or due to the coexistence of cubic
 201 and tetragonal phases, t is averaged over these regions. As explained in Supplementary section 3,
 202 the presence of preferred orientation in our $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ perovskite films results in some
 203 uncertainty in the absolute value of the tilt angle. This would manifest as a systematic change in the
 204 magnitude of the tilt angle (e.g., shifted higher or lower by some constant multiplier) but will not
 205 impact our conclusions, as relative changes are not affected.

206 The temperature evolution of the tilt angle, t , is shown in figure 3a for all $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$
 207 compositions along with comparable tilt angle temperature dependence for pure compounds, including
 208 MAPbI₃ films [50] and MAPbBr₃ single crystals. To aid comparison, we have plotted t as a function
 209 of $T - T_0$, where for $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ films T_0 is the temperature where the average tilt goes
 210 to zero, and for MAPbI₃ films and MAPbBr₃, T_0 is the phase transition temperature. The results
 211 shown in figure 3a for MAPbI₃ and MAPbBr₃ are consistent with the literature [60, 61, 62, 63,
 212 59]. The striking qualitative observation from figure 3a is that the **tilt evolution** at the transition in
 213 all the mixed A-site, halide $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ compositions is significantly broadened compared

214 to MAPbI_3 films and MAPbBr_3 , which as we explain below, is a manifestation of compositional
215 heterogeneity. This behavior is most apparent for 40-17 and 17-05 where we have the largest temper-
216 ature range. For all our alloyed compositions, figure 3a shows that the slopes of the tilt angle t versus
217 temperature T are much smaller than it is for the pure compounds MAPbI_3 and MAPbBr_3 , consistent
218 with the broadened transition although there is a few $^{\circ}\text{C}$ offset in the tilt for 17-17, 25-20 and 40-30
219 (compared to 40-17), reflecting the errorbar in determining T_0 . For some compositions (17-17, 25-20
220 and 40-30), the temperature range is limited since we are unable to cool the films.

221 As noted in the introduction, we do not distinguish between intrinsic (thermodynamic phase co-
222 existence) and extrinsic compositional heterogeneity. Hence, we model the phase transition behavior
223 in figure 3a as a smeared first order or second-order transition. For a first order behavior, the intrinsic
224 temperature dependence is a step function at T_c ; while for the second-order transition, the behavior
225 near the transition follows a power-law of the form $t \sim (T_c - T)^{\beta}$, where β is the critical exponent for
226 the phase transition and T_c is the transition temperature. For either type of transition, we account for
227 the impact of compositional heterogeneity by convoluting the intrinsic temperature dependence (step
228 function or power-law) with a Gaussian distribution of transition temperatures. Both fitting processes
229 are discussed in detail in Supplementary section 4. For $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$, the step function
230 and power-law fits give a T_c at 73°C and 80°C , respectively, with a broad width due to the distribu-
231 tion of transition temperatures (52°C and 45°C , respectively). The best fit value for β is 0.49, but
232 with large uncertainty. We observe qualitatively similar behavior in all of the $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$
233 compositions studied and report T_c , fitting transition width, and T_0 values in table 1, while figure 3b
234 plots T_0 for different compositions. Note that our experimental data set only allows us to determine
235 a T_c and transition width for $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ and $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.05}\text{I}_{0.95})_3$, as data are
236 only available above room temperature and for $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.05}\text{I}_{0.95})_3$, we can only set a lower
237 limit on the transition width of 21°C .

238 This behaviour is different from pure compounds, MAPbI_3 and MAPbBr_3 . Despite being a well-
239 studied system, the character of the tetragonal-to-cubic phase transition in MAPbI_3 is still debated.
240 DFT calculations suggest that the transition is second-order [64], but several experimental studies
241 have concluded that the transition is closer to tricritical (mean field exponent $\beta = 0.25$) [60, 62,
242 63, 65]. A recent study of the tetragonal-to-cubic transition in a deuterated MAPbI_3 single crystal
243 indicates that the transition is at least weakly first order with small tetragonal domains nucleating

Table 1: Phase transition temperatures T_c and T_0 and fitting temperature transition width for the smeared first order behavior, for the compositions studied herein. Note that for $y = 17$, $x = 5$, the limited temperature range may result in an overestimated T_c and underestimated transition width.

[Cs], y (%)	[Br], x (%)	T_0 (°C)	T_c (°C)	transition width (°C)
17	05	53	39	> 21
17	17	37		
25	20	56		
40	17	97	73	45
40	30	64		

244 near iodide vacancies in the cubic lattice [66].

245 For $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$, we observe a very small increase in the FWHM of the $t(210)$ Bragg peak
246 about 10 to 20 °C below T_0 , as shown in figure 3c. This weak dependence is, in general, inconsistent
247 with the expected power-law increase in FWHM [67] for a second-order transition. This observation
248 suggests that the tetragonal-to-cubic transition in our $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ films is not second order.

249 Lattice parameter behavior

250 The temperature dependence of the lattice parameters through the phase transition provides insight
251 into the phase behavior and nature of the heterogeneity that broadens the transition. Figure 4a
252 shows the temperature evolution of the lattice parameters a' and c as well as the pseudo-cubic lat-
253 tice parameter d for $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ and $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.05}\text{I}_{0.95})_3$. We used the $t(210)$
254 and $t(201)$ peaks to extract the lattice parameters, and for ease of comparison, we plot $a' = a/\sqrt{2}$
255 and $d = (a'^2 c)^{\frac{1}{3}}$. These lattice parameters are thus reflective of only the regions that are tetra-
256 gonal within the film. It is informative to compare this dependence to that for the pure compound
257 MAPbI_3 [60], which is shown in figure 4b, and behaves the same as the pure compound MAPbBr_3
258 [61]. Before making this comparison, we calculate that the volumetric thermal expansion coeffi-
259 cients (β_V) for $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ and $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.05}\text{I}_{0.95})_3$ as $(2.11 \pm 0.1) \times 10^{-4} \text{ K}^{-1}$ and
260 $(1.83 \pm 0.3) \times 10^{-4} \text{ K}^{-1}$, respectively. These values are slightly larger than $\beta_V = (1.52 \pm 0.07) \times 10^{-4} \text{ K}^{-1}$
261 for $\text{Cs}_{0.15}\text{FA}_{0.85}\text{PbI}_3$ [68], and suggest that Br in the X site gives a larger β_V compared to I. We observe
262 no change in β_V at the phase transition (T_0 in figure 4a).

263 There is a distinct difference in the lattice parameter behavior near the transition for $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$
264 and MAPbI_3 in that for the pure compound a' and c converge approaching the transition temperature,
265 but for the mixed-cation, mixed halide perovskite a' and c diverge approaching T_0 , especially c . We

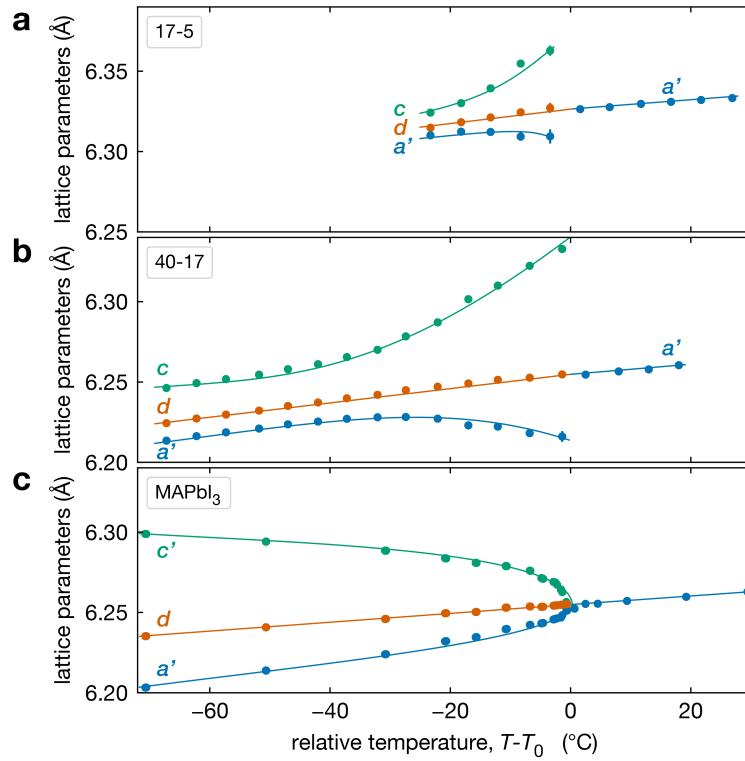


Figure 4: Evolution of lattice parameters for $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.05}\text{I}_{0.95})_3$ (a), $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ (b) and MAPbI_3 (c) plotted as a function of the relative temperature $T - T_0$. (a-b) The parameters are extracted from the tetragonal peak positions. c) Data extracted from ref [60]. Here $a' = a/\sqrt{2}$ (blue), $d = (a'^2 c)^{\frac{1}{3}}$ (brown) and c (green). For MAPbI_3 we plot $c' = c/2$ instead. Above T_0 , the structure is cubic, so only a single lattice parameter is shown. Solid lines show the general trend.

propose the following explanation for this unusual observation for $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ perovskite films. This divergent behavior is a manifestation of the compositional heterogeneity and the resulting distribution of transition temperatures. Figure 3c and Table 1 show that $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ with high Br and/or low Cs will transform into the cubic phase at lower temperatures than for low Br and/or high Cs. Consequently, as temperature increases, regions of the $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ films with high Br and/or low Cs will transform first into the cubic phase and the tetragonal regions of the film will be those that are richer in Cs or poor in Br. Since the tetragonal $t(210)$ and $t(201)$ peaks are used to determine a' and c in figure 4a, these lattice parameters will increasingly correspond to regions of low Br and/or high Cs. Figure 4a shows c increasing approaching T_0 , and these still tetragonal regions must have relatively more I, the larger halide, thus driving the larger c . Although indirect, this suggests that there is more heterogeneity in the halide composition than for the A-site cation. We expand on this hypothesized behavior in Supplementary section 5 with a simple model

278 with four regions with different compositions. Overall, these observations on the lattice parameters
279 support our conclusion on compositional heterogeneity broadening the transition and point to the
280 halides as more heterogeneous.

281 **Band gap temperature dependence**

282 To better understand how this tetragonal-to-cubic transition might influence the operation of solar
283 cells, we measured the optical band gap as a function of temperature. We measured the external
284 quantum efficiency (EQE) of an optimized $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ device at three temperatures
285 on either side of T_0 (temperature where the material is fully cubic) and extracted the band gap
286 by fitting the low energy tail of the EQE at each temperature (see Supplementary section 6). The
287 extracted optical band gaps are plotted in figure 5. We observe that below T_0 the band gap decreases
288 with temperature, and above T_0 , the band gap increases with temperature. While both trends are
289 modest, they are distinguishable.

290 In the low-temperature tetragonal phase, the average tilt angle decreases upon heating, increasing
291 the overlap of the orbitals associated with the Pb–X bonds, decreasing the band gap [69, 70, 71,
292 72], consistent with figure 5. In the cubic phase above T_0 , the band gap increases with temperature,
293 consistent with DFT calculations that show that the band gaps of biaxially strained cubic CsPbI_3
294 and CsSnI_3 increase with strain [70]. This is because in the cubic phase, lattice expansion reduces
295 the orbital overlap, increasing the band gap [69, 70, 71, 72].

296 We fit the decreasing and increasing band gap regimes with linear dependence and find that
297 their intersection at 38°C is nearly identical to the value of $T_0 = 37^\circ\text{C}$ that we estimate from XRD
298 data, see figure 3b. These results (figure 5) coupled with our map of the transition temperature
299 (figure 3b) can be used to estimate the temperature where the slope in the band gap vs temperature
300 changes from negative to positive (between about T_c and T_0). A positive slope for the band gap vs
301 temperature results in a comparatively more efficient solar cell at higher temperatures than for a
302 negative slope. Thus, the temperature where this slope changes may have important implications for
303 the temperature coefficient for power conversion efficiency in MHP solar cells, if this is near typical
304 operational temperatures.

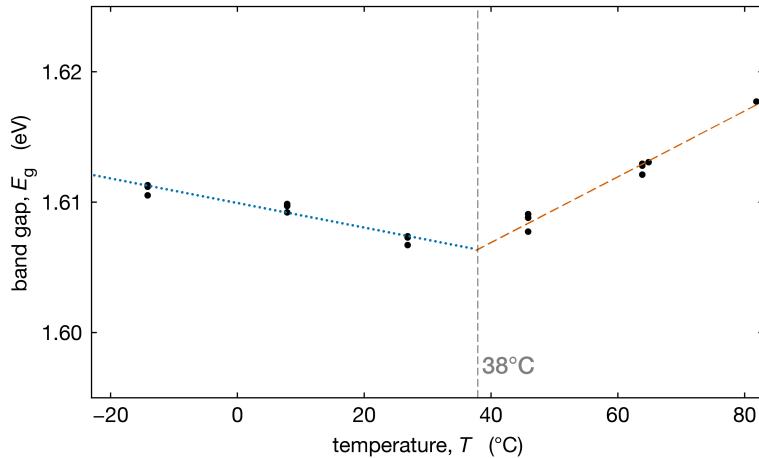


Figure 5: Band gap (eV) (black dots) for perovskite composition $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ as a function of temperature ($^{\circ}\text{C}$), calculated from up and downward cycles of EQE, with a linear fit before discontinuity (blue dashed line) and after slope discontinuity (red dotted line). The grey dashed line shows the intersection of the two slopes.

305 Discussion

306 Relative to the pure phases, we have observed two distinct differences in the phase transition behavior
 307 for multi-cation, multi-halide MHPs. First, as reflected in the octahedral tilt angle, the transition is
 308 broadened over a considerable temperature range of the order of $40\text{ }^{\circ}\text{C}$. Second, the behavior of the
 309 lattice parameters of the tetragonal domains just below the transition diverges slightly as opposed to
 310 converging in the pure compounds. These behaviors are consistent with the presence of compositional
 311 heterogeneity.

312 With respect to the phase transition behavior, we have defined two characteristic temperatures.
 313 T_0 is the temperature at which the average tilt angle becomes zero and the entirety of the film adopts
 314 the cubic structure. T_c is the average transition temperature obtained from fitting the temperature
 315 dependence of the tilt angle to a broadened transition. While we cannot distinguish compositional
 316 heterogeneity as intrinsic (or thermodynamic) or extrinsic (processing-induced), T_0 and T_c have differ-
 317 ent meanings for these scenarios. For the case of two-phase coexistence, with increasing temperature,
 318 the film evolves from pure tetragonal to cubic plus tetragonal to pure cubic [38]. Here, T_0 is a solvus
 319 temperature, while T_c is near the middle of the two-phase region. In the case of extrinsic heterogene-
 320 ity, T_0 corresponds to the transition temperature for regions with the highest transition temperature
 321 and T_c is the transition temperature reflective of the average composition. In either case the breadth
 322 of the transition, as obtained from either the fit transition width (See Supplementary section 2.3) or

323 the difference between T_0 and T_c , is indicative of the compositional heterogeneity and can be used to
324 provide an estimate of these inhomogeneities. With reference to figure 3b, which shows the variation
325 in T_0 with Cs and Br composition, a 30 to 40 °C change corresponds to roughly 10 to 15 % variation
326 in either Cs or Br composition. This suggests compositional variation of the order 10 to 15 %, which
327 is considerable.

328 There are additional ways that the phase transition might be broadened, in particular, the com-
329 pound can be relaxor ferroelectric or dipolar glass. In this case, a homogeneous solid solution would
330 transform upon cooling from a non-polar paraelectric to an ergodic relaxor state with polar nanore-
331 gions. This can eventually lead to vanishing or quenching the phase transition [73]. While some studies
332 pointed out that MHP alloys can present these responses [74, 75], this is not the case in our work
333 because (a) the P4/mmb tetragonal phase is not consistent with an ergodic relaxor or dipolar glass
334 [73], (b) there is no evidence of ordered A or X sites, (c) at the temperature of our experiments
335 (>300 K), freezing out-of-rotational motions in the organics does not occur and (d) we constantly
336 observe a phase transition throughout our compositional space

337 From figure 3b, we find that at fixed Br substitution, T_0 increases with increasing Cs substitution,
338 and at fixed Cs substitution, T_0 decreases with increasing Br substitution. The room temperature
339 phase map reported by Beal *et al.* suggests that for higher degrees of Cs substitution, more Br
340 substitution is required before any tetragonal phase is observed [14]. This is because Cs is a smaller
341 cation than FA, and Br is a smaller anion than I. Structurally, Br substitution shrinks the size of the
342 cuboctahedral cavity so that it is a better fit for Cs, and the Goldschmidt tolerance factor τ_G is closer
343 to unity [39]. Thus, when the amount of Br in the lattice is increased, more Cs can be substituted
344 into the cubic crystal lattice before any distortion in the form of octahedral rotations is required to
345 decrease the size of the cuboctahedral cavity [14]. This structural argument is also supported by
346 DFT calculations, which confirm that the energy of the tetragonal phase is lower in systems where
347 the A-site cation is small relative to its cuboctahedral cavity ($\tau_G < 1$) [55].

348 A compositional variation of 10 to 15 % is significant. It is reasonable to expect that this should
349 lead to broadening of the XRD peaks of the order 0.5 to 1 % of the peak Q value (e.g., 0.005 \AA^{-1}
350 - 0.01 \AA^{-1} for the $t(110)/(002)$ peak). This is estimated from the variation in lattice parameters
351 with composition [35, 37] and the compositional differences estimated above. This prediction is less
352 than the observed XRD peak widths of the $t(110)/(002)$ and $t(200)/(112)$ fundamental XRD peaks

353 of about 0.005 \AA^{-1} and 0.006 \AA^{-1} , respectively. One explanation of this apparent discrepancy is
354 that regions of different composition are partly coherently strained to have similar or equal lattice
355 parameters throughout the film; this would imply that the regions with varied composition are small
356 in order to achieve such lattice coherency. This explanation would result in smaller peak widths than
357 predicted from the estimated compositional variations, consistent with our data. In $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$,
358 prior work has shown a miscibility gap with strong intergrowth of I-rich and Br-rich crystallites
359 and unexpected deviations from Vegard's law [35]. These observations also may be related to the
360 possibility of coherency strain.

361 Conclusion

362 We used synchrotron XRD to characterize the crystal structure of $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites
363 across the tetragonal-to-cubic phase transition. We find that, in contrast to MAPbI_3 , which has an
364 out-of-phase octahedral tilt pattern, $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites have an in-phase pattern of
365 octahedral rotations about the *c*-axis. This symmetry gives rise to superlattice reflections in the XRD
366 patterns that we use to calculate the temperature dependence of the octahedral tilt angle and lattice
367 parameters across the transitions. Our results show that the tetragonal to cubic transition occurs
368 over a broad range of temperatures that we identify as due to compositional heterogeneity leading to
369 coexisting cubic and tetragonal regions. These give rise to a range of local transition temperatures
370 that effectively smear out into the global transition. We estimate the local compositional variations
371 of about 10 to 15 % in either or both FA/Cs and Br/I, although the data suggest more in the halide.
372 We also find that the temperature dependence of the band gap changes sign from negative to positive
373 near the temperature where the MHP structure becomes cubic, which is explained as a competition
374 between lattice expansion and lead-halide bond length changes due to varying tilt angle.

375 Our results support and complement previous works demonstrating that multi-anion, multi-cation
376 MHP films can be compositionally heterogeneous at the nanoscale. Furthermore, we have established
377 a simple methodology to characterize this compositional heterogeneity in mixed anion, cation MHP.
378 Using this methodology can enable a way to understand the extent and impact of heterogeneity on
379 the properties and performance of MHP photovoltaic materials.

380 **Experimental data**

381 **Device fabrication & characterisation** Films were prepared using the standard chlorobenzene
382 antisolvent method with in a 4:1 dimethylformamide (DMF)/dimethyl sulfoxide solvent (DMSO)
383 mixture that was optimized for film morphology at each composition and is detailed in ref [14]. After
384 spin casting, films were annealed on a hotplate at 60 °C for 1 min and subsequently at 105 °C for 30
385 min under an N₂ atmosphere. Two-dimensional X-ray scattering was collected with monochromatic
386 12.7 keV synchrotron beam and recorded on 255 mm² × 255 mm² detector, under a flowing He atmo-
387 sphere. Images were calibrated using LaB₆ and integrated to 1D using PyFAI[76]. Tilt angle was
388 obtained following the method developed in Supplementary sections 2 and 3. EQE was measured in
389 a cryostat on solar cells made with the following stack: Glass, ITO, NiOx, Perovskite, PCBM, ALD
390 SnO₂, Sputtered ITO. Light was shone through the Sputtered ITO side.

391 **MAPbBr₃ crystallization and single crystal X-ray diffraction** MAPbBr₃ crystals were pre-
392 pared by inverse temperature crystallization. A 1 M solution of PbBr₂ and MABr in DMF was
393 prepared and passed through a 0.22 µm filter; the filtered solution was heated to 82 °C in an oil bath
394 and removed after 30 min. MAPbBr₃ crystals were isolated quickly from the cooling mother liquor
395 to avoid re-dissolution. Crystals were mounted on an X-ray transparent MiTeGen microloop using
396 Paratone oil and single crystal X-ray diffraction was performed on a Bruker D8 Venture diffractometer
397 equipped with a Photon 100 CMOS detector. The temperature was varied from 100 to 300 K with
398 an Oxford Cryostream.

399 Data were collected from ϕ and ω scans using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The frames
400 were integrated using SAINT V8.38A and absorption correction was performed with SADABS-2016/2,
401 both implemented in the Bruker APEX 3 software. Space group determination was performed with
402 XPREP, with space group assignment based on reported structures, systematic absences, $|E * E - 1|$
403 statistics, and refinement statistics. The structure was solved using direct methods with the SHELXT
404 software [77] and refined using a least-squares method implemented by SHELXL-2014/7 in the Olex
405 2 software package.

406 The Pb and Br thermal displacement parameters are refined anisotropically, whereas the C, N,
407 and H parameters are refined isotropically. Due to the well-known dynamic cation disorder in the
408 tetragonal and cubic phases, the methylammonium (MA) molecule was refined two ways: as a single

409 atom centered in the interstices, or as a molecule confined to reside along high symmetry directions
410 determined by residual electron densities. Additional constraints to the MA cation were applied
411 to the C–N bond length (1.47 Å) and to fix fractional occupancy to maintain stoichiometry. No
412 significant differences were observed in the final structures refined with these two methods.

413 **Conflicts of interest** There are no conflicts of interest to declare

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426 **Author contributions**

427 **Conceptualization:** JB, AGP, MFT

428 **Data curation:** JB, AGP, JAV

429 **Formal analysis:** JB, JAV, LW, NJW, ZZ

430 **Investigation:** REB, AFN (sample prep), AGP, JAV, LW, LTS (XRD), EW (EQE)

431 **Methodology:** JB, AGP, MFT, JAV, LW, NJW, ZZ

432 **Supervision:** LTS, AFN, MDM, MFT

433 **Validation:** JAV, LW, NJW, ZZ

434 **Visualisation:** JB, ZZ

435 **Writing – original draft:** JB, REB

References

1. Manser JS, Christians JA, and Kamat PV. Intriguing optoelectronic properties of metal halide perovskites. *Chemical reviews* 2016; 116:12956–3008. DOI: 10.1021/acs.chemrev.6b00136
2. Fu Y, Zhu H, Chen J, Hautzinger MP, Zhu XY, and Jin S. Metal halide perovskite nanostructures for optoelectronic applications and the study of physical properties. *Nature Reviews Materials* 2019; 4:169–88. DOI: 10.1038/s41578-019-0080-9
3. Eperon GE, Leijtens T, Bush KA, Prasanna R, Green T, Wang JTW, McMeekin DP, Volonakis G, Milot RL, and May R. Perovskite-perovskite tandem photovoltaics with optimized band gaps. *Science* 2016; 354:861–5. DOI: 10.1126/science.aaf9717
4. Kovalenko MV, Protesescu L, and Bodnarchuk MI. Properties and potential optoelectronic applications of lead halide perovskite nanocrystals. *Science* 2017; 358:745–50. DOI: 10.1126/science.aam7093
5. Sahli F, Werner J, Kamino BA, Bräuninger M, Monnard R, Paviet-Salomon B, Barraud L, Ding L, Leon JJD, and Sacchetto D. Fully textured monolithic perovskite/silicon tandem solar cells with 25.2% power conversion efficiency. *Nature materials* 2018 :1. DOI: 10.1038/s41563-018-0115-4
6. Xu J, Boyd CC, Zhengshan JY, Palmstrom AF, Witter DJ, Larson BW, France RM, Werner J, Harvey SP, Wolf EJ, et al. Triple-halide wide-band gap perovskites with suppressed phase segregation for efficient tandems. *Science* 2020; 367:1097–104. DOI: 10.1026/science.aaz5074
7. NREL. Best research-cell efficiency chart. <https://www.nrel.gov/pv/cell-efficiency.html>. accessed Feb 2021. 2020
8. Green MA, Dunlop ED, Hohl-Ebinger J, Yoshita M, Kopidakis N, and Ho-Baillie AW. Solar cell efficiency tables (Version 55). *Progress in Photovoltaics: Research and Applications* 2020; 28:3–15. DOI: 10.1002/pip.3371
9. Correa-Baena JP, Saliba M, Buonassisi T, Grätzel M, Abate A, Tress W, and Hagfeldt A. Promises and challenges of perovskite solar cells. *Science* 2017; 358:739–44. DOI: 10.1126/science.aam6323
10. Snaith HJ. Present status and future prospects of perovskite photovoltaics. *Nature materials* 2018; 17:372–6. DOI: 10.1038/s41563-018-0071-z
11. Soto-Montero T, Soltanpoor W, and Morales-Masis M. Pressing challenges of halide perovskite thin film growth. *APL materials* 2020; 8:110903. DOI: 10.1063/5.0027573
12. Leijtens T, Bush KA, Prasanna R, and McGehee MD. Opportunities and challenges for tandem solar cells using metal halide perovskite semiconductors. *Nature Energy* 2018; 3:828–38. DOI: 10.1038/s41560-018-0190-4
13. Hoke ET, Slotcavage DJ, Dohner ER, Bowring AR, Karunadasa HI, and McGehee MD. Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. *Chemical Science* 2015; 6:613–7. DOI: 10.1039/C4SC03141E

14. Beal RE, Hagström NZ, Barrier J, Gold-Parker A, Prasanna R, Bush KA, Pasarello D, Schelhas L, Brüning K, Steinrück HG, McGehee MD, Toney MF, and Nogueira AF. Structural origins of light-induced phase segregation in organic-inorganic halide perovskite photovoltaic materials. *Matter* 2020; 2:1–13. DOI: [10.1016/j.matt.2019.11.001](https://doi.org/10.1016/j.matt.2019.11.001)
15. Knight AJ and Herz LM. Preventing phase segregation in mixed-halide perovskites: a perspective. *Energy & Environmental Science* 2020; 13:2024–46. DOI: [10.1039/d0ee00788A](https://doi.org/10.1039/d0ee00788A)
16. Brennan MC, Ruth A, Kamat PV, and Kuno M. Photoinduced anion segregation in mixed halide perovskites. *Trends in Chemistry* 2020; 2:282–301. DOI: [10.1016/j.trechm.2020.01.010](https://doi.org/10.1016/j.trechm.2020.01.010)
17. Eames C, Frost JM, Barnes PR, O’regan BC, Walsh A, and Islam MS. Ionic transport in hybrid lead iodide perovskite solar cells. *Nature communications* 2015; 6:1–8. DOI: [10.1038/ncomms8497](https://doi.org/10.1038/ncomms8497)
18. Walsh A and Stranks SD. Taking control of ion transport in halide perovskite solar cells. *ACS Energy Letters* 2018; 3:1983–90. DOI: [10.1021/acsenergylett.8b00764](https://doi.org/10.1021/acsenergylett.8b00764)
19. Senocrate A and Maier J. Solid-state ionics of hybrid halide perovskites. *Journal of the American Chemical Society* 2019; 141:8382–96. DOI: [10.1021/jacs.8b13594](https://doi.org/10.1021/jacs.8b13594)
20. Schelhas LT, Li Z, Christians JA, Goyal A, Kairys P, Harvey SP, Kim DH, Stone KH, Luther JM, Zhu K, et al. Insights into operational stability and processing of halide perovskite active layers. *Energy & Environmental Science* 2019; 12:1341–8. DOI: [10.1039/C8EE03051K](https://doi.org/10.1039/C8EE03051K)
21. Bush KA, Frohna K, Prasanna R, Beal RE, Leijtens T, Swifter SA, and McGehee MD. Compositional engineering for efficient wide band gap perovskites with improved stability to photoinduced phase segregation. *ACS Energy Letters* 2018; 3:428–35. DOI: [10.1021/acsenergylett.7b01255](https://doi.org/10.1021/acsenergylett.7b01255)
22. Barker AJ, Sadhanala A, Deschler F, Gandini M, Senanayak SP, Pearce PM, Mosconi E, Pearson AJ, Wu Y, Srimath Kandada AR, et al. Defect-assisted photoinduced halide segregation in mixed-halide perovskite thin films. *ACS Energy Letters* 2017; 2:1416–24. DOI: [10.1021/acsenergylett.7b00282](https://doi.org/10.1021/acsenergylett.7b00282)
23. Bischak CG, Sanehira EM, Precht JT, Luther JM, and Ginsberg NS. Heterogeneous Charge Carrier Dynamics in Organic-Inorganic Hybrid Materials: Nanoscale Lateral and Depth-Dependent Variation of Recombination Rates in Methylammonium Lead Halide Perovskite Thin Films. *Nano Lett.* 2015; 15(7):4799–807. DOI: [10.1021/acs.nanolett.5b01917](https://doi.org/10.1021/acs.nanolett.5b01917)
24. Bischak CG, Hetherington CL, Wu H, Aloni S, Ogletree DF, Limmer DT, and Ginsberg NS. Origin of Reversible Photoinduced Phase Separation in Hybrid Perovskites. *Nano Lett.* 2017; 17:1028–33. DOI: [10.1021/acs.nanolett.6b04453](https://doi.org/10.1021/acs.nanolett.6b04453)
25. Bischak CG, Wong AB, Lin E, Limmer DT, Yang P, and Ginsberg NS. Tunable Polaron Distortions Control the Extent of Halide Demixing in Lead Halide Perovskites. *J. Phys. Chem. Lett.* 2018; 9:3998–4005. DOI: [10.1021/acs.jpcllett.8b01512](https://doi.org/10.1021/acs.jpcllett.8b01512)
26. Wieghold S, Tresback J, Correa-Baena JP, Hartono NTP, Sun S, Liu Z, Layurova M, VanOrman ZA, Bieber AS, Thapa J, Lai B, Cai Z, Nienhaus L, and Buonassisi T. Halide Heterogeneity Affects Local Charge Carrier Dynamics in Mixed-Ion Lead Perovskite Thin Films. *Chem. Mater.* 2019; 31:3712?3721. DOI: [10.1021/acs.chemmater.9b00650](https://doi.org/10.1021/acs.chemmater.9b00650)
27. Quilettes DW de, Vorpahl SM, Stranks SD, Nagaoka H, Eperon GE, Ziffer ME, Snaith HJ, and Ginger DS. Impact of microstructure on local carrier lifetime in perovskite solar cells. *Science* 2015; 348:683–6. DOI: [10.1126/science.aaa5333](https://doi.org/10.1126/science.aaa5333)

28. Correa-Baena JP, Luo Y, Brenner TM, Snaider J, Sun S, Li X, Jensen MA, Hartono NTP, Nienhaus L, Wieghold S, et al. Homogenized halides and alkali cation segregation in alloyed organic-inorganic perovskites. *Science* 2019; 363:627–31. DOI: [10.1126/science.aah5065](https://doi.org/10.1126/science.aah5065)
29. Szostak R, Silva J, Turren-Cruz SH, Soares M, Freitas R, Hagfeldt A, Tolentino H, and Nogueira A. Nanoscale mapping of chemical composition in organic-inorganic hybrid perovskite films. *Science advances* 2019; 5:eaaw6619. DOI: [10.1126/sciadv.aaw6619](https://doi.org/10.1126/sciadv.aaw6619)
30. Tennyson EM, Doherty TAS, and Stranks SD. Heterogeneity at multiple length scales in halide perovskite semiconductors. *Nat. Rev. Mater.* 2019; 4:573–87. DOI: doi.org/10.1038/s41578-019-0125-0
31. Gratia P, Grancini G, Audinot JN, Jeanbourquin X, Mosconi E, Zimmermann I, Dowsett D, Lee Y, Grätzel M, De Angelis F, et al. Intrinsic halide segregation at nanometer scale determines the high efficiency of mixed cation/mixed halide perovskite solar cells. *Journal of the American Chemical Society* 2016; 138:15821–4. DOI: [10.1021/jacs.6b10049](https://doi.org/10.1021/jacs.6b10049)
32. Mishra SK, Gupta MK, Mittal R, Zbiri M, Rols S, Schober H, and Chaplot SL. Phonon dynamics and inelastic neutron scattering of sodium niobate. *Phys. Rev. B* 2014 May; 89(18):184303. DOI: [10.1103/PhysRevB.89.184303](https://doi.org/10.1103/PhysRevB.89.184303)
33. Charles B, Weller MT, Rieger S, Hatcher LE, Henry PF, Feldmann J, Wolverson D, and Wilson CC. Phase Behavior and Substitution Limit of Mixed Cesium-Formamidinium Lead Triiodide Perovskites. *Chemistry of Materials* 2020; 32:2282–91. DOI: [10.1021/acs.chemmater.9b04032](https://doi.org/10.1021/acs.chemmater.9b04032)
34. Mohanty A, Swain D, Govinda S, Row TNG, and Sarma D. Phase Diagram and Dielectric Properties of $MA_{1-x}FA_xPbI_3$. *ACS Energy Letters* 2019; 4:2045–51. DOI: [10.1021/acsenergylett.9b01291](https://doi.org/10.1021/acsenergylett.9b01291)
35. Lehmann F, Franz A, Többens DM, Levcenco S, Unold T, Taubert A, and Schorr S. The phase diagram of a mixed halide (Br, I) hybrid perovskite obtained by synchrotron X-ray diffraction. *RSC advances* 2019; 9:11151–9. DOI: [10.1039/C8RA09398A](https://doi.org/10.1039/C8RA09398A)
36. Kim SY, Lee HC, Nam Y, Yun Y, Lee SH, Kim DH, Noh JH, Lee JH, Kim DH, Lee S, and Heo YW. Ternary diagrams of the phase, optical bandgap energy and photoluminescence of mixed-halide perovskites. *Acta Materialia* 2019; 81:460–9. DOI: <https://doi.org/10.1016/j.actamat.2019.10.008>
37. Li Z, Yang M, Park JS, Wei SH, Berry JJ, and Zhu K. Stabilizing perovskite structures by tuning tolerance factor: formation of formamidinium and cesium lead iodide solid-state alloys. *Chemistry of Materials* 2016; 28:284–92. DOI: [10.1021/acs.chemmater.5b04107](https://doi.org/10.1021/acs.chemmater.5b04107)
38. Bechtel JS and Van der Ven A. First-principles thermodynamics study of phase stability in inorganic halide perovskite solid solutions. *Physical Review Materials* 2018; 2:045401. DOI: [10.1103/PhysRevMaterials.2.045401](https://doi.org/10.1103/PhysRevMaterials.2.045401)
39. Goldschmidt VM. Die gesetze der krystallochemie. *Naturwissenschaften* 1926; 14:477–85. DOI: [10.1007/BF01507527](https://doi.org/10.1007/BF01507527)
40. Stokes HT, Kisi EH, Hatch DM, and Howard CJ. Group-theoretical analysis of octahedral tilting in ferroelectric perovskites. *Acta Crystallographica Section B* 2002 Dec; 58:934–8. DOI: [10.1107/S0108768102015756](https://doi.org/10.1107/S0108768102015756)
41. Glazer A. The classification of tilted octahedra in perovskites. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* 1972; 28:3384–92. DOI: [10.1107/S0567740872007976](https://doi.org/10.1107/S0567740872007976)

42. Cochran W. Crystal Stability and the Theory of Ferroelectricity. *Phys. Rev. Lett.* 1959 Nov; 3(9):412–4. DOI: [10.1103/PhysRevLett.3.412](https://doi.org/10.1103/PhysRevLett.3.412)
43. Woodward PM. Octahedral tilting in perovskites. I. Geometrical considerations. *Acta Crystallographica Section B* 1997; 53:32–43. DOI: [10.1107/S0108768196010713](https://doi.org/10.1107/S0108768196010713)
44. Woodward PM. Octahedral tilting in perovskites. II. Structure stabilizing forces. *Acta Crystallographica Section B* 1997; 53:44–66. DOI: [10.1107/S0108768196012050](https://doi.org/10.1107/S0108768196012050)
45. Aleksandrov K. The sequences of structural phase transitions in perovskites. *Ferroelectrics* 1976; 14:801–5. DOI: [10.1080/00150197608237799](https://doi.org/10.1080/00150197608237799)
46. Bechtel JS and Van der Ven A. Octahedral tilting instabilities in inorganic halide perovskites. *Phys. Rev. Materials* 2018 Feb; 2(2):025401. DOI: [10.1103/PhysRevMaterials.2.025401](https://doi.org/10.1103/PhysRevMaterials.2.025401)
47. Zhong W and Vanderbilt D. Competing Structural Instabilities in Cubic Perovskites. *Phys. Rev. Lett.* 1995 Mar; 74(13):2587–90. DOI: [10.1103/PhysRevLett.74.2587](https://doi.org/10.1103/PhysRevLett.74.2587)
48. Gopalan V and Litvin DB. Rotation-reversal symmetries in crystals and handed structures. *Nature materials* 2011; 10:376. DOI: [10.1038/nmat2987](https://doi.org/10.1038/nmat2987)
49. Bartel CJ, Sutton C, Goldsmith BR, Ouyang R, Musgrave CB, Ghiringhelli LM, and Scheffler M. New tolerance factor to predict the stability of perovskite oxides and halides. *Science advances* 2019; 5:eaav0693. DOI: [10.1126/sciadv.aav0693](https://doi.org/10.1126/sciadv.aav0693)
50. Schelhas LT, Christians JA, Berry JJ, Toney MF, Tassone CJ, Luther JM, and Stone KH. Monitoring a silent phase transition in $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells via operando X-ray diffraction. *ACS Energy Letters* 2016; 1:1007–12. DOI: [10.1021/acsenergylett.6b00441](https://doi.org/10.1021/acsenergylett.6b00441)
51. Cowley RA. Lattice Dynamics and Phase Transitions of Strontium Titanate. *Phys. Rev.* 1964 May; 134(4A):A981–A997. DOI: [10.1103/PhysRev.134.A981](https://doi.org/10.1103/PhysRev.134.A981)
52. Shirane G and Yamada Y. Lattice-Dynamical Study of the 110°K Phase Transition in SrTiO_3 . *Phys. Rev.* 1969 Jan; 177(2):858–63. DOI: [10.1103/PhysRev.177.858](https://doi.org/10.1103/PhysRev.177.858)
53. Harada J, Axe JD, and Shirane G. Neutron-Scattering Study of Soft Modes in Cubic BaTiO_3 . *Phys. Rev. B* 1971 Jul; 4(1):155–62. DOI: [10.1103/PhysRevB.4.155](https://doi.org/10.1103/PhysRevB.4.155)
54. Salje EKH, Gallardo MC, Jiménez J, Romero FJ, and Cerro J del. The cubic-tetragonal phase transition in strontium titanate: excess specific heat measurements and evidence for a near-tricritical, mean field type transition mechanism. *Journal of Physics: Condensed Matter* 1998 Jun; 10:5535–43. DOI: [10.1088/0953-8984/10/25/006](https://doi.org/10.1088/0953-8984/10/25/006)
55. Young J and Rondinelli JM. Octahedral rotation preferences in perovskite iodides and bromides. *The journal of physical chemistry letters* 2016; 7:918–22. DOI: [10.1021/acs.jpclett.6b00094](https://doi.org/10.1021/acs.jpclett.6b00094)
56. Weber OJ, Ghosh D, Gaines S, Henry PF, Walker AB, Islam MS, and Weller MT. Phase behavior and polymorphism of formamidinium lead iodide. *Chemistry of Materials* 2018; 30:3768–78. DOI: [10.1021/acs.chemmater.8b00862](https://doi.org/10.1021/acs.chemmater.8b00862)
57. Ghosh D, Smith AR, Walker AB, and Islam MS. Mixed a-cation perovskites for solar cells: atomic-scale insights into structural distortion, hydrogen bonding, and electronic properties. *Chemistry of Materials* 2018; 30:5194–204. DOI: [10.1021/acs.chemmater.8b01851](https://doi.org/10.1021/acs.chemmater.8b01851)
58. Francisco-López A, Charles B, Alonso MI, Garriga M, Campoy-Quiles M, Weller MT, and Goñi AR. Phase Diagram of Methylammonium/Formamidinium Lead Iodide Perovskite Solid Solutions from Temperature-Dependent Photoluminescence and Raman Spectroscopies. *The Journal of Physical Chemistry C* 2020; 124:3448–58. DOI: [10.1021/acs.jpcc.9b10185](https://doi.org/10.1021/acs.jpcc.9b10185)

59. Franz A, Többens DM, Lehmann F, Kärgell M, and Schorr S. The influence of deuteration on the crystal structure of hybrid halide perovskites: a temperature-dependent neutron diffraction study of FAPbBr_3 . *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials* 2020; 76. DOI: [10.1107/S2052520620002620](https://doi.org/10.1107/S2052520620002620)

60. Kawamura Y, Mashiyama H, and Hasebe K. Structural Study on Cubic?Tetragonal Transition of $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Journal of the Physical Society of Japan* 2002; 71:1694–7. DOI: [10.1143/JPSJ.71.1694](https://doi.org/10.1143/JPSJ.71.1694)

61. Mashiyama H, Kawamura Y, Magome E, and Kubota Y. Displacive Character of the Cubic-Tetragonal Transition in $\text{CH}_3\text{NH}_3\text{PbX}_3$. *J. Korean Phys. Soc.* 2003 Apr; 42(April):S1026–S1029

62. Comin R, Crawford MK, Said AH, Herron N, Guise WE, Wang X, Whitfield PS, Jain A, Gong X, McGaughey AJH, and Sargent EH. Lattice dynamics and the nature of structural transitions in organolead halide perovskites. *Phys. Rev. B* 2016 Sep; 94(9):094301. DOI: [10.1103/PhysRevB.94.094301](https://doi.org/10.1103/PhysRevB.94.094301)

63. Whitfield P, Herron N, Guise W, Page K, Cheng Y, Milas I, and Crawford M. Structures, phase transitions and tricritical behavior of the hybrid perovskite methyl ammonium lead iodide. *Scientific reports* 2016; 6:35685. DOI: [10.1038/srep35685](https://doi.org/10.1038/srep35685)

64. Brivio F, Frost JM, Skelton JM, Jackson AJ, Weber OJ, Weller MT, Goñi AR, Leguy AMA, Barnes PRF, and Walsh A. Lattice dynamics and vibrational spectra of the orthorhombic, tetragonal, and cubic phases of methylammonium lead iodide. *Phys. Rev. B* 2015; 92. DOI: [10.1103/PhysRevB.92.144308](https://doi.org/10.1103/PhysRevB.92.144308)

65. Cordero F, Trequattrini F, Craciun F, Paoletti A, Pennesi G, and Zanotti G. Cation reorientation and octahedral tilting in the metal-organic perovskites MAPI and FAPI. *Journal of Alloys and Compounds* 2020 :158210. DOI: [10.1016/j.jallcom.2020.158210](https://doi.org/10.1016/j.jallcom.2020.158210)

66. Weadock NJ, Gehring PM, Gold-Parker A, Smith IC, Karunadasa HI, and Toney MF. On the question of dynamic domains and critical scattering in cubic methylammonium lead triiodide. *Physical Review Letters* 2020; 125:075701. DOI: [10.1103/PhysRevLett.125.075701](https://doi.org/10.1103/PhysRevLett.125.075701)

67. Ru N, Condron C, Margulis G, Shin K, Laverock J, Dugdale S, Toney M, and Fisher I. Effect of chemical pressure on the charge density wave transition in rare-earth tritellurides R Te 3. *Physical Review B* 2008; 77:035114. DOI: [10.1103/PhysRevB.77.035114](https://doi.org/10.1103/PhysRevB.77.035114)

68. Abdelsamie M, Xu J, Bruening K, Tassone CJ, Steinrück HG, and Toney MF. Impact of Processing on Structural and Compositional Evolution in Mixed Metal Halide Perovskites during Film Formation. *Advanced Functional Materials* 2020 Jul; 30:2001752. DOI: [10.1002/adfm.202001752](https://doi.org/10.1002/adfm.202001752)

69. Chang Y, Park C, and Matsuishi K. First principles study of the structural and the electronic properties of the lead-halide-based inorganic-organic perovskites $(\text{CH}_3\text{NH}_3)\text{PbX}_3$ and CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). *Journal of the Korean Physical Society* 2004; 44(4):889–93

70. Grote C and Berger RF. Strain tuning of tin–halide and lead–halide perovskites: a first-principles atomic and electronic structure study. *The Journal of Physical Chemistry C* 2015; 119:22832–7. DOI: [10.1021/acs.jpcc.5b07446](https://doi.org/10.1021/acs.jpcc.5b07446)

71. Lee JH, Bristowe NC, Lee JH, Lee SH, Bristowe PD, Cheetham AK, and Jang HM. Resolving the physical origin of octahedral tilting in halide perovskites. *Chemistry of Materials* 2016; 28:4259–66. DOI: [10.1021/acs.chemmater.6b00968](https://doi.org/10.1021/acs.chemmater.6b00968)

72. Prasanna R, Gold-Parker A, Leijtens T, Conings B, Babayigit A, Boyen HG, Toney MF, and McGehee MD. Band gap tuning via lattice contraction and octahedral tilting in perovskite materials for photovoltaics. *Journal of the American Chemical Society* 2017; 139:11117–24. DOI: [10.1021/jacs.7b04981](https://doi.org/10.1021/jacs.7b04981)
73. Bokov AA and Ye ZG. Recent progress in relaxor ferroelectrics with perovskite structure. *Journal of Materials Science* 2006; 41:31–52
74. Mozur EM, Hope MA, Trowbridge JC, Halat DM, Daemen LL, Maughan AE, Prisk TR, Grey CP, and Neilson JR. Cesium Substitution Disrupts Concerted Cation Dynamics in Formamidinium Hybrid Perovskites. *Chemistry of Materials* 2020; 32:6266–77
75. Simenas M, Balciunas S, Wilson JN, Svirskas S, Kinka M, Garbaras A, Kalendra V, Gagor A, Szewczyk D, Sieradzki A, et al. Suppression of phase transitions and glass phase signatures in mixed cation halide perovskites. *Nature communications* 2020; 11:1–9
76. Kieffer J and Karkoulis D. PyFAI, a versatile library for azimuthal regrouping. *Journal of Physics: Conference Series*. IOP Publishing. 2013 :202012. DOI: [10.1088/1742-6596/425/20/202012i](https://doi.org/10.1088/1742-6596/425/20/202012i)
77. Sheldrick GM. SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallographica Section A: Foundations and Advances* 2015; 71:3–8. DOI: [10.1107/S2053273314026370](https://doi.org/10.1107/S2053273314026370)