Are Mixed-Halide Ruddlesden–Popper Perovskites Really Mixed?

Stefano Toso,* Irina Gushchina, Allen G. Oliver, Liberato Manna, and Masaru Kuno

ABSTRACT: Mixing bromine and iodine within lead halide perovskites is a common strategy to tune their optical properties. This comes at the cost of instability, as illumination induces halide segregation and degrades device performances. Hence, understanding the behavior of mixed-halide perovskites is crucial for applications. In 3D perovskites such as MAPb(Br\(_{1-x}\)I\(_x\))\(_3\) (MA = methylammonium), all of the halide crystallographic sites are similar, and the consensus is that bromine and iodine are homogeneously distributed prior to illumination. By analogy, it is often assumed that Ruddlesden–Popper layered perovskites such as (BA)\(_2\)MAPb(Br\(_{1-x}\)I\(_x\))\(_3\) (BA = butylammonium) behave alike. However, these materials possess a much wider variety of halide sites featuring diverse coordination environments, which might be preferentially occupied by either bromine or iodine. This leaves an open question: are mixed-halide Ruddlesden–Popper perovskites really mixed? By combining powder and single-crystal diffraction experiments, we demonstrate that this is not the case: bromine and iodine in RP perovskites preferentially occupy different sites, regardless of the crystallization speed.

Ruddlesden–Popper (RP) lead halide perovskites are a class of two-dimensional (2D) semiconductors that have recently gained relevance as promising candidates for optoelectronic and photovoltaic applications.\(^1\)\(^-\)\(^6\) Described by the formula L\(_2\)A\(_{n-1}\)Pb\(_n\)X\(_{3n+1}\), they consist of \(n\) two-dimensional layers of corner-sharing [PbX\(_6\)]\(^{4-}\) octahedra (\(X = \text{Cl, Br, I}\)) held together by isotropic cations (\(A = \text{Cs}\), methylammonium (MA), formamidinium (FA), ...). Individual layers, in turn, are separated by long-chain ammonium cations such as butylammonium (L = BA) or phenylethylammonium (L = PEA).\(^3\)

A demand for band gap tuning, electronic structure engineering, and integration into three-dimensional (3D) perovskite solar cells is now extending interest to mixed bromide–iodide RP perovskites, L\(_2\)A\(_{n-1}\)Pb\(_n\)Br\(_{1-x}\)I\(_x\))\(_3\)\(_{n+1}\), where \(x\) indicates the bromine fraction. Recent reports confirm that mixing halides in RP perovskites offers additional control over their optical properties\(^8\) and enables the use of a wider variety of L cations in comparison to single-halide RP perovskites.\(^9\) Other studies have demonstrated the creation of vertical and horizontal heterojunctions, obtained by stacking premade RP sheets\(^10\) or by exploiting halide-diffusion reactions.\(^11\)

Despite progress in the area, applications of 2D mixed-halide perovskites are limited by photoinduced anion segregation. Recent investigations into their photostability highlight a tendency of halide anions to migrate within crystals under illumination,\(^12\)-\(^14\) similar to what is observed in 3D mixed-halide APb(Br\(_{1-x}\)I\(_x\))\(_3\) perovskites.\(^12\)-\(^13\) In this regard, photo-induced anion segregation appears to be an intrinsic instability of lead halide perovskites as a whole.

As early studies shed light on the behavior of mixed-halide RP perovskites under external stimuli, questions have arisen about their properties when at rest. Indeed, while the structures of 3D mixed-halide perovskites are well described as halide alloys,\(^15\)-\(^16\) there are reasons to believe that the situation is more complex in 2D mixed-halide RP perovskites. Compared to 3D perovskites, RP structures offer a greater diversity of halide crystallographic sites. Of these, some sites are embedded deep within inorganic layers (central sites, Ct), while others protrude directly into the organic cation layers (apical sites, Ap) or alternatively create extended horizontal networks that form the inorganic layers (equatorial sites, Eq).

This diversity of coordination environments may therefore promote the occupation of certain sites by different anions, by virtue of differences in ionic radii or interaction affinities with cations. Recently reported theoretical predictions bring arguments to support such preferential positioning of halides in (PEA)\(_2\)Pb(Br\(_{1-x}\)I\(_x\))\(_4\).\(^8\) These results are corroborated by single-crystal X-ray diffraction studies on (ter-BA)\(_2\)Pb(Br\(_{0.5}\)I\(_{0.5}\))\(_4\).\(^9\) The same effect has also been reported for other...
layered metal halides such as (MA)$_2$Cu(Cl$_{1-x}$Br$_x$)$_4$. This suggests that lead-based mixed-halide RP perovskites do not behave as ideal alloys when it comes to placing I in the structure. To rationalize this behavior, we therefore construct a geometric model (Figure 2) that relates RP unit cell parameters to the distribution of halide anions in different crystallographic sites (Ap, Ct, and Eq). The model is therefore construct a geometric model (Figure 2) that relates RP unit cell parameters to the distribution of halide anions in different crystallographic sites (Ap, Ct, and Eq). The model is

![Figure 1](https://pubs.acs.org/doi/abs/10.1021/acsenergylett.2c01967)

**Figure 1.** PXRD characterization of (BA)$_2$MAPb$_2$(Br$_{1-x}$I$_x$)$_7$. (a) (top) Optical microscopy image of (BA)$_2$MAPb$_2$(Br$_{1-x}$I$_x$)$_7$ crystals. (bottom) SEM image of a representative crystal, with overlaid lattice vectors. (b) PXRD patterns of (BA)$_2$MAPb$_2$(Br$_{1-x}$I$_x$)$_7$ samples. Highlighted are the (0120) peaks, whose shift toward lower angles highlights the anomalous unit cell expansion along the b cell axis for mixed-halide compositions. (c) Le Bail profile fit of the (BA)$_2$MAPb$_2$I$_7$ PXRD pattern. Vertical dotted gray lines indicate the family of (02k0) peaks typical of RP perovskites. Some (hkh) peaks, which ensure a reliable determination of the $a^*$ parameter, have also been indexed.

Sample compositions have been verified using scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM-EDX). All mixed-halide specimens were found to be significantly richer in iodine than expected from their stock solution feed ratios. This indicates a tendency of RP structures to incorporate iodine over bromine. A calibration curve, relating measured experimental compositions to those of starting precursor solutions, was therefore constructed (see Figure S1 in the Supporting Information). In what follows, sample compositions are labeled using $x_{\text{tot}} = \text{Br}/[\text{Br + I}]$, where Br and I are the measured halide atomic fractions: $x_{\text{tot}} = 0$ stands for pure-iodide samples, while $x_{\text{tot}} = 1$ stands for pure-bromide samples.

All samples were characterized via PXRD (Figure 1b). Their diffraction patterns feature a series of intense and periodic (02k0) peaks, typical of RP perovskites (see also Figure S2 in the Supporting Information). A Le Bail profile fit was performed on all patterns (Figure 1c shows it for $x = 0$; other fits are available in Figure S3 in the Supporting Information) to trace how unit cell parameters change with halide composition. Because RP perovskites are pseudotetragonal materials, most reflections that differentiate $a$ and $c$ (i.e., $h \neq l$) are weak and overlap strongly. This makes their individual measurements unreliable. In contrast, a pseudotetragonal $a^*$ parameter that represents the average of $a$ and $c$ is easily determined, based on strong and well-resolved (hkh) reflections.

As expected, $a^*$ decreases linearly from $a^* = 8.92$ Å for $x = 0$ to $a^* = 8.33$ Å for $x = 1$ (Figure 2a). The $b$ parameter, however, does not change linearly with halide composition (Figure 2b). Rather, it first rises and then falls, reaching a maximum at $x_{\text{tot}} = 0.5$ ($b = 39.9$ Å). This behavior is foreshadowed in Figure 1b by the marked shift of (02k0) peaks toward lower angles. Together, $a^*$ and $b$ result in a monotonic decrease of the unit cell volume ($V_{\text{cell}} = a^*b^*c^*$) as $x_{\text{tot}}$ increases from 0 to 1 (Figure 2c). Only a mild positive inflection is seen due to the nonlinear behavior of $b$. Such an anomalous dependence of $b$ on the halide composition suggests that lead-based mixed-halide RP perovskites do not behave as ideal alloys when it comes to placing I$^-$ and Br$^-$ in the structure. To rationalize this behavior, we therefore construct a geometric model (Figure 2) that relates RP unit cell parameters to the distribution of halide anions in different crystallographic sites (Ap, Ct, and Eq). The model is...
Figure 2. Impact of halide distribution on (BA)$_2$MAPb$_7$X$_7$ unit cell parameters. (a–c) Experimental RP unit cell parameters (black asterisks) and model predictions (colored lines). (d) Halide distribution in apical (Ap), equatorial (Eq), and central (Ct) sites, corresponding to parameters predicted in (a)–(c). (e) Visual representation of the model, showing how $a^*$ and $b$ are functions of bond lengths and tilt angles, and of the organic cation spacing $L$. The inorganic layer thickness, $d$, is defined in eq 2. In (d) and (e), red, blue, and purple identify Ap, Eq, and Ct sites, respectively.

Lead–halide bond lengths ([Pb–X]) are modeled as linear combinations of limiting [Pb–Br] and [Pb–I] bond distances, as measured by single-crystal X-ray diffraction (SCXRD) on (BA)$_2$MAPb$_7$Br$_7$ and (BA)$_2$MAPb$_7$I$_7$, weighted by the fractional occupation of respective halide sites (Table S2). In eqs 1 and 2, the subscripts Eq and Ct identify the site involved in each [Pb–X] bond and the bond itself. Similarly, $\alpha$ and $\beta$ are estimated from limiting values determined by SCXRD (Table S3). We additionally note that octahedral tilting modes adopted by pure-bromide and pure-iodide structures are incompatible. $^{7,21}$ We therefore assume that a transition structure at $x_{tot} = 0.5$ does not experience octahedral tilt in any direction. This assumption is later proven correct. Finally, $L$ is estimated by assuming that the volume occupied by butylammonium chains remains constant in all structures (see the Supporting Information and Table S4 for further discussion). A detailed description of the model and explanations of how [Pb–X], $\alpha$, $\beta$, and $L$ depend on the halide composition of Ap, Eq, and Ct sites can be found in Figure S4 in the Supporting Information.

The only free variable in the model is $x_{eq}$. Indeed, given the similarity to bulk halide sites in 3D perovskites, Ct sites are assumed to be occupied by $I^−$ and Br$^−$ with no preference (i.e., $x_{eq} \approx x_{tot}$). Consequently, $x_{eq}$ is a function of $x_{tot}$ ($x_{eq} = 3x_{tot} - 2x_{Ap}$ from eq 3). With this, PXRD-extracted $b$ values (Figure 2b) are fit using the model by varying $x_{eq}$. The fit simultaneously yields model-predicted $a^*$ and $V_{cell}$ values that can be further compared with experiments (Figure 2a,c) to assess the model’s overall performance.

Solid colored lines in Figure 2 reveal that the model captures the linear trend of $a^*$ in Figure 2a, the peaked behavior of $b$ in Figure 2b, and the mild positive inflection of $V_{cell}$ in Figure 2c as $x_{tot}$ increases from 0 to 1. These results correspond to a marked excess of iodine in unit cell apical positions and bromine in equatorial positions. The trend is observed over the entire (BA)$_2$MAPb$_7$(Br$_{1-x}$I$_{x}$)$_7$ composition range (Figure 2d).

As a point of reference, for $x_{tot} = 0.5$ the halide distribution predicted by the model is $Ap = 23\%$ Br, $Eq = 62\%$ Br, and $Ct = 50\%$ Br.

Overall, these results demonstrate that the anisotropic unit cell expansion observed by PXRD arises from a preferential positioning of halide anions. Such an expansion is rationalized as the combination of two effects. First, the prevalence of larger $I^−$ ions in apical positions results in an elongation of [Pb–I] bonds parallel to the unit cell $b$ axis. Second, the prevalence of smaller Br$^−$ ions in equatorial positions shrinks the lattice on the $a$–$c$ plane. This laterally compresses the BA cations and forces them to expand along the $b$ axis. What results is an increase of the interlayer distance, $L$. This conclusion is corroborated by SCXRD-solved structures of (BA)$_2$MAPb$_7$Br$_7$ and (BA)$_2$MAPb$_7$I$_7$, where $L = 13.49$ Å in the former and $L = 13.15$ Å in the latter. As both effects are solely dependent on [Pb–X] bond distances, the behavior is expected to be general across RP structures made using different organic cations.

Furthermore, the anisotropic expansion along $b$ measured as a bowing in the position of PXRD (02kθ) reflections, appears to be a reliable approach for detecting the preferential positioning of halide anions in mixed-halide RP structures. Indeed, further simulations (Figure S5) indicate that the $b$ parameter could grow as much as +4.3% if halides displayed full preferentiality for apical and equatorial sites and would instead decrease by −1.3% if halides were randomly alloyed.

In the model, unit cell parameters $a^*$ and $b$ are functions of [Pb–X] bond lengths, of horizontal and vertical octahedra tilt angles ($\alpha$ and $\beta$), and of the organic cation layers thickness $L$ (eqs 1 and 2). All parameters in eqs 1 and 2 depend on the halide occupation of Ap, Eq, and Ct sites, which are related to each other and to experimentally established sample halide compositions, $x_{tot}$, via the material stoichiometry (eq 3).

$$a^* = \frac{4[Pb−X]_{eq} \sin(\frac{\alpha}{2})}{\sqrt{2}} \quad (1)$$
$$b = 2L + 4d = 2L + 4[Pb−X]_{ct} \sin(\frac{\alpha}{2}) \quad (2)$$
$$x_{tot} = \frac{4}{7}x_{eq} + \frac{2}{7}x_{ap} + \frac{1}{7}x_{ct} \quad (3)$$

Semiquantitatively and rationalizes the observed PXRD structural trends summarized in Figure 2a–c.
crystal composition of $x_{\text{tot}} = 0.56$ (Table S5). Those results are very close to the halide distribution predicted by the geometric model for $x = 0.5$. A complementary analysis of halide site occupation via electron densities confirms the same trend and suggests a more marked preference of apical and central sites for iodine (Ap, 7% Br, 93% I; Ct, 37% Br, 63% I; Eq, 64% Br, 36% I). The extracted crystal composition is $x_{\text{tot}} = 0.44$, again compatible within error with the target $x_{\text{tot}} = 0.5$ composition (Table S6).

Overall, both PXRD and SCXRD data point to a preferential positioning of $I^-$ and $Br^-$ anions in lead-based mixed-halide RP structures. Discrepancies in determined occupancies likely stem from a combination of model assumptions (e.g., $x_{\text{tot}} \approx x_{\text{hal}}$) approach biases (bond lengths vs electron density), and crystallization speeds. The last point is especially relevant, given that sample preparation methods might influence the crystallization dynamics and therefore the distribution of anions within mixed-halide RP structures. However, both PXRD and SCXRD showed clear evidence of preferential halide positioning and crystallization occurred over minutes and hours, respectively. Therefore, the question arises whether faster crystallization conditions might favor a more homogeneous halide distribution. To address this question, we have collected XRD patterns of $n = 2$ (BA)$_2$MAPb$_7$(Br$_{1-x}$I$_x$)$_7$ and $n = 1$ (BA)$_2$Pb$_7$(Br$_{1-x}$I$_x$)$_7$ RP perovskite thin films prepared by spin coating (Figures S6 and S7). The latter $n = 1$ specimens are of particular interest, given extensive prior investigations of these materials.$^8,9,12,13$ Details of the thin-film spin-coating synthesis have been provided in the Supporting Information.

For both $n = 1$ and $n = 2$ thin films, Figure 4 shows clear nonlinear $b$ dependences with halide composition. This confirms that halide sites in mixed-halide RP perovskites are preferentially occupied even under the fast crystallization conditions often adopted for fabricating samples and devices.$^{17-19,15-17}$ Notably, both $n = 1$ and $n = 2$ samples demonstrate comparable maximum expansions along $b$ ($n = 1$, $+1.58\%$; $n = 2$, $+1.73\%$).
Figure 4. Cell parameter $b$ in thin films. (a) Experimental $b$ parameter measured on $n = 2$ (top) and $n = 1$ (bottom) thin films prepared by spin coating. (b) Structure schemes of $n = 2$ (BA)$_2$MAPb$_2$Br$_7$ (top) and $n = 1$ (BA)$_2$PbX$_4$ (bottom) RP perovskites.

To conclude, the common assumption that anions in mixed-halide perovskites are homogeneously distributed at the unit cell level, which holds for 3D perovskites because their halide sites share comparable chemical environments,$^{15,16,23–25}$ does not apply to RP layered perovskites. In RP perovskites, instead, $\Gamma^{-}$ anions preferentially occupy apical sites that are closest to long-chain organic cations, while $\text{Br}^{-}$ anions prefer to reside in equatorial sites, surrounded by lead cations. This preferential positioning occurs regardless of the crystallization speed and is likely due to the different ionic radii of iodine and bromine. Our conclusions are supported by recent reports on lead-based mixed-halide RP perovskites$^{9,17,26}$ and appear to be part of a broader trend that extends beyond the field of lead-based materials, wherein structural anisotropy emerges to inhibit halide alloying.$^{17–19,27,28}$

Although the effect of such an inhomogeneous halide distribution on the optoelectronic properties of mixed-halide RP perovskites has yet to be fully investigated, there are reasons to believe that it might not be negligible. Indeed, we demonstrated that mixed-halide RP samples can adopt altered symmetry and octahedral tilting modes compared to pure-halide RP specimens. This might affect the orbital overlap and thus the electronic structure of these materials. Moreover, being aware of preferential anion occupation in mixed-halide RP structures might assist in better understanding the recent observations of anion photosegregation in these materials.

**ASSOCIATED CONTENT**

*Supporting Information* (PDF) C(CIF) The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsenergylett.2c01967](https://pubs.acs.org/doi/10.1021/acsenergylett.2c01967).

Synthesis and characterization methods, oriented- and powder-XRD patterns of (BA)$_2$MAPb$_2$(Br$_{1-x}$I$_x$)$_7$ polycrystalline samples and Le Bail fits of the latter, outline of the RP structure geometric model, discussion of SCXRD analyses, additional characterization of spin-coated thin films (PDF)

Crystallographic information files of the (BA)$_2$MAPb$_2$Br$_7$, (BA)$_2$MAPb$_2$I$_7$, and the (BA)$_2$MAPb$_2$(Br$_{0.5}$I$_{0.5}$)$_7$ structures solved by SCXRD (ZIP)

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Notes

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