

Br-Induced Suppression of Low-Temperature Phase Transitions in Mixed Cation Mixed Halide Perovskites

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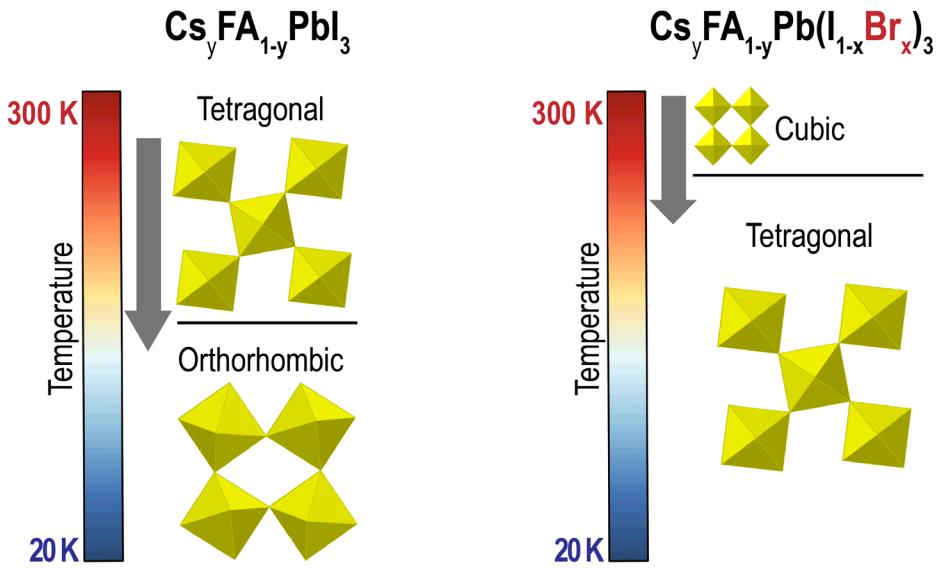
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Abstract

Mixed-cation mixed-halide lead perovskites have shown to be excellent candidates for solar energy conversion. However, understanding the structural phases of these mixed-ion perovskites across a wide range of operating temperatures, including very low temperatures for space applications, is crucial. In this study, we investigated the structure of formamidinium-based $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ using low-temperature *in-situ* synchrotron powder X-ray diffraction. Our findings revealed that substituting the I anion with Br in mixed-cation (Cs,FA) perovskites suppressed the phase transformation from tetragonal to orthorhombic at low temperatures. The addition of Br also prevented the formation of non-perovskite secondary phases. We gained fundamental insights into the structural behavior of these materials by creating a low-temperature phase diagram for the compositional set of mixed-cation mixed-halides. This understanding of the structural properties lays the groundwork for designing more robust and efficient energy materials capable of functioning under extreme temperature conditions, including space-based solar energy conversion.

Introduction

Mixed-cation mixed-halide lead halide perovskites (LHP) have emerged as promising materials for solar energy conversion.¹ Specifically, formamidinium(FA)-rich compositions have demonstrated higher thermal stability and an optimal bandgap for single-junction solar cells.² Compositional mixing has been employed to achieve optimal optoelectronic properties and stability.^{3,4} However, it is crucial to unravel the structural phases across a wide range of operating temperatures, including very low temperatures relevant to space applications, to ensure the proper functioning and stability of these materials. The most common and efficient compositions include mixing cesium (Cs) and FA in the A-site, as well as iodine (I) and bromine (Br) in the X-site, resulting in $(\text{Cs,FA})\text{Pb}(\text{I,Br})_3$ LHP compositions. A knowledge gap exists on a complete phase diagram for both mixed-cation and mixed-halide compositions. In this work, we aim to construct a low-temperature phase diagram for (Cs,FA) mixed halide (I,Br) perovskites.

Previous studies have reported low-temperature phase diagrams for single-ion compositions such as FAPbI_3 ,⁵ CsPbI_3 ,⁶ FAPbBr_3 ,⁷ and CsPbBr_3 .⁸ Generally, perovskites exhibit a cubic (α) phase at high temperatures above a certain threshold. As the temperature decreases, the perovskite structure undergoes phase transitions from cubic to tetragonal (β) and then from tetragonal to orthorhombic (γ) phase. Phase diagrams have also been studied for single-cation/mixed-halide or mixed-cation/single-halide compositions. For instance, Lehmann et al. investigated and presented the temperature phase diagram for $\text{MAPb}(\text{I,Br})_3$ compositions, highlighting the two phase transitions.⁹ Nasstrom et al. reported the high-temperature phase diagram for $\text{CsPb}(\text{I,Br})_3$, observing different phase transitions during heating and cooling.¹⁰ Other studies focused on the phase diagram for the mixed-cation iodide-based perovskites, either $(\text{MA,FA})\text{PbI}_3$ ¹¹ or $(\text{Cs,FA})\text{PbI}_3$.^{12,13} In the first,¹¹ they used Raman spectroscopy and

photoluminescence to uncover different low-temperature phase transitions dependent on the FA content, related to its higher symmetry compared to MA. In the latter, for (Cs,FA) perovskite, the authors revealed the cubic-tetragonal-orthorhombic transitions and solubility limit of the Cs:FA ratio to form a pure perovskite phase.^{12,13}

In the case of pure Br-based compositions, it has been demonstrated that Cs substitution in FAPbBr₃ perovskite suppresses the orthorhombic phase transition at low temperatures attributed to a geometric blocking associated with the rotation of FA molecules.¹⁴ The suppression of the orthorhombic phase at low temperatures has also been observed in mixed cation MA-dimethylammonium (DMA) lead bromide perovskites (MA,DMA)PbBr₃.^{15,16} This suppression was attributed to the increased disorder of the organic cations in the mixed samples, leading to higher symmetry and less distortion of the inorganic framework. The improved structural stability also enhanced their photodetection capabilities.¹⁶ Despite the knowledge from studying low-temperature phase transitions in various cation and halide combinations, a complete structural phase diagram for the widely-used and highly efficient LHPs (Cs,FA)Pb(I,Br)₃ is still lacking.

Herein, we study the crystal structure of FA-based lead halide perovskite compositions Cs_yFA_{1-y}Pb(Br_xI_{1-x})₃ by low-temperature *in-situ* synchrotron powder X-ray diffraction (XRD) from 300 K down to 23 K. Our focus was on FA-rich and I-rich compositions to maintain a low bandgap suitable for single-junction solar cells. Our findings reveal that the low-temperature orthorhombic phase transition is suppressed as Br replaces I in the mixed-cation LHP compositions. Additionally, the inclusion of Br eliminates secondary non-perovskite phases. We construct three halide-dependent temperature phase diagrams for different Cs concentrations, demonstrating that adding Br to the mixed-cation (Cs,FA) system stabilizes the higher symmetry perovskite structure from room to low temperatures, and prevents the formation of non-perovskite

phases. This fundamental understanding of the perovskite structure in a wide range of temperatures provides a basis for designing and developing more resilient and efficient materials capable of functioning under extreme conditions. Comprehending the state-of-the-art halide perovskite's structure across the entire temperature range is paramount.

Results and discussion

Properties and Structure at Room Temperature and 300 K

To investigate the low-temperature phase transitions for different FA-based LHP compositions, we selected a mixed-cation and mixed-halide compositional space $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ as shown in **Figure1A**. We chose this compositional space to have FA-rich compositions with ideal bandgaps for single-junction solar cells.^{2,5,17} The selected upper limit for Cs was 17 % molar, given that its thermodynamic limit to form a single-phase perovskite when mixed with FA is around 15%^{12,13,18} and 20% molar.¹⁹ Therefore, we chose 17 %, targeting a single-phase perovskite formation. The upper limit chosen for Br was 17 %, keeping an I-based composition and equaling the maximum added percent of Cs.

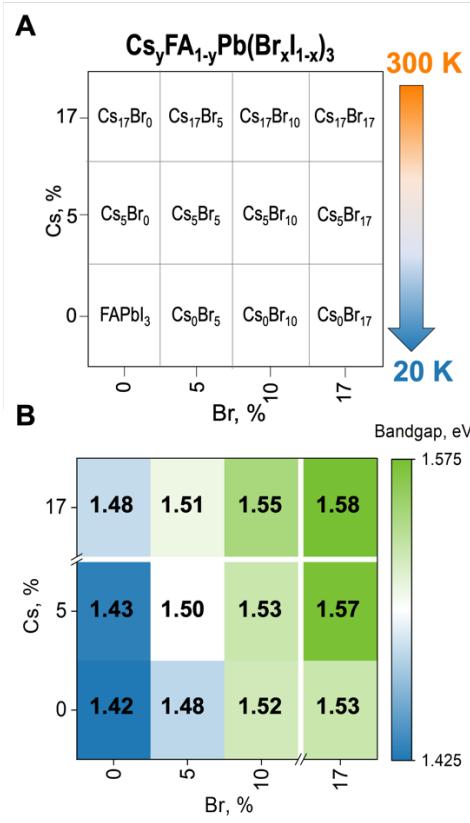


Figure 1. Mixed-cation and mixed-halide perovskite compositions of study. (A) Selected compositions to study the in-situ phase transitions from 300 K to 23 K, **(B)** Bandgap from UV-VIS at room temperature

Bandgap tunability is one of the main advantages of LHPs.²⁰ To analyze the optoelectronic properties of the synthesized materials, we measured UV-VIS absorption spectroscopy (at room temperature), and used the Tauc-plot method (**Figure S1**) to calculate the optical bandgap.²¹ In **Figure 1B**, the lowest experimental bandgap is 1.42 eV for the pure FAPbI_3 , which is close but lower than other reported values from calculations (1.51 eV),²² absorbing in the range to achieve the maximum theoretical power conversion efficiency for single-junction solar cells according to the Shockley-Queisser limit.²³ However, FAPbI_3 perovskite is unstable at room temperature and ambient atmosphere, transforming into a yellow powder with a hexagonal structure, identified here as 2H. For this reason, pure FAPbI_3 is not further analyzed in this work. The LHP's bandgap increased as Cs and Br were added to the FA-based compositions (**Figure 1B**). Both cation and halide substitution in FAPbI_3 reduces the crystal structure's lattice parameters, resulting in

increased bandgap, as described and experimentally shown for the complete set of (Cs,FA) and (I,Br) compositions by An and others.²⁰ We observe that adding Br increases the bandgap further compared to the Cs addition. It has been demonstrated that the bandgap and lattice parameters of semiconducting materials correlate with the effective anion radius of the halides, in this case, Br.²⁴ Whereas the A-site cation does not participate in the band edge states, it does influence the room temperature optical properties indirectly through changes to the structure by the octahedral tilting and arrangement^{16,25} We highlight that one of the main advantages of LHPs is their property tunability through compositional engineering, as we see here on bandgap tunability when we add Cs and Br. In this case, the studied compositions have a bandgap from 1.43 eV to 1.58 eV, remaining in an ideal range for high-efficiency single-junction perovskite solar cells.

To study the crystal structure of these LHPs, we performed powder XRD, as shown in **Figure 2**. In **Figure 2A** we show the structure of the perovskite phase at 300 K, corresponding to either a cubic phase of space group $Pm\bar{3}m$ (α) or to a tetragonal phase of space group $P4/mbm$ (β). We analyzed in detail the XRD patterns at 300 K (**Figure 2B**) by Le bail refinements (**Figure S2-4**). From this initial analysis, we identified the structural phases present for each composition, as shown in **Figure 2C**, where α is an orange square, and β is a green rectangle. All the studied compositions without Br, Cs_xBr_0 , are β phase at 300 K. This structure is similar to the work by An and others,²⁰ where $(Cs_{17},FA_{83})PbI_3$ was tetragonal at room temperature, and with the work by Charles and coworkers¹² where $(Cs_{10},FA_{90})PbI_3$ was tetragonal at 290 K. Adding Cs to FAPbI₃ structure induces a chemical pressure or lattice strain effect due to the Cs and FA cation size mismatch, leading to a structural distortion, stronger FA-iodide hydrogen bonding interaction, and symmetry breaking.²⁶ Therefore, the symmetry break when adding Cs explains the initial β phase for Cs_xBr_0 . Adding only 5% Br to the Cs_{17} perovskite phase ($Cs_{17}Br_5$) also results in a β structure.

This low amount of Br does not change the tetragonal structure, suggesting that since there is no octahedral tilting, there are also no changes in cation rotation. However, adding more Br (10 % and 17 %) leads to an initially cubic perovskite structure (α) at room temperature.⁵ Previous work by Johnston and coworkers showed that adding up to 15% Br to (Cs,MA,FA)PbI₃ suppressed the organic cation rotation, enhancing long-lived carrier lifetimes. In this case, we suggest that adding 10 % or 17 % of Br would similarly cause a decrease in cation rotation, leading to a higher symmetry α perovskite.

Beyond the perovskite structural analysis, we also identified secondary non-perovskite phases from the powder XRDs in **Figure 2**. Single-cation CsPbI₃ or FAPbI₃ form non-perovskites phases with either face- or edge-sharing octahedra. Hexagonal face-sharing FAPbI₃, referred to here as 2H, is a face-sharing octahedra structure with space group *P6₃/mmc* and the orthorhombic edge-sharing CsPbI₃, known as δ_{Cs} , has a space group *Pnma* (**Figure 2A**).^{27,28} There are also other intermediate hexagonal polytypes between the corner-sharing and the pure face-sharing, known as 4H or 6H.^{27,29} These hexagonal polytypes (H) are present in mixed halides. **Figure 2C** summarizes the secondary phases at 300 K, showing the hexagonal polytypes H as hexagons and the δ_{Cs} as triangles. All compositions Cs₀Br_x show some hexagonal polytypes, specifically due to their characteristic diffraction peaks between 8 and 12 $^{\circ}$ in 2 θ of the diffraction pattern (**Figure 2B**). For Cs₅Br₀, we observe the formation of some non-perovskite δ_{Cs} , possibly due to phase segregation.¹² For Cs₅Br₅, some polytype H phases are observed, but remarkably, in Cs₅Br₁₀ and Cs₅Br₁₇, no secondary phases are formed. The work by Gratia and others²⁷ shows that around 3% Cs is fundamental in FA-rich (I,Br) compositions to increase the structural chemical pressure, inhibiting the formation of polytypes, explaining why Cs is needed in (I,Br) compositions for improved stability and symmetry. Additionally, the work by Li,¹³ Charles,¹² Mozur,¹⁴ and Ghosh,²⁶

show the importance of adding Cs up to 15 – 20% (solubility limit) since above this value, the mixed-cation LHP will phase segregate into their two phase single-cation non-perovskite phases. In the case of $\text{Cs}_{17}\text{Br}_x$, we overpass this solubility limit. Therefore, all $\text{Cs}_{17}\text{Br}_x$ compositions show the presence of the δ_{Cs} phase (**Figure 2B**). Herein, we see how a combination of adding less than 17 % Cs and more than 5% Br ($\text{Cs}_5\text{Br}_{10}$, and $\text{Cs}_5\text{Br}_{17}$), in both cases, leads to the desired combination for a single-phase high symmetry structure.

Lastly, from the powder XRD at 300 K and the Le Bail analysis, we determined the lattice parameters and calculated the unit cell volume (**Figure 2D**). Tetragonal structures have the lattice parameters $a = b \neq c$. In the case of cubic structures, the lattice parameters are all equal $a = b = c$. The volume for the tetragonal structure is significantly larger, given that the value of a and b is around 8.96 Å, increasing the overall volume of the tetragonal unit cell. For the cubic unit cell volumes, we observe that the volume decreases as Cs and Br are added in FAPbI_3 . Given the replacement by both smaller-size ions, the overall cubic unit cell volume is expected to decrease. A smaller size cation, Cs^+ , is replacing the larger cation FA^+ as the halide Br^- is replacing a larger ion, I^- .

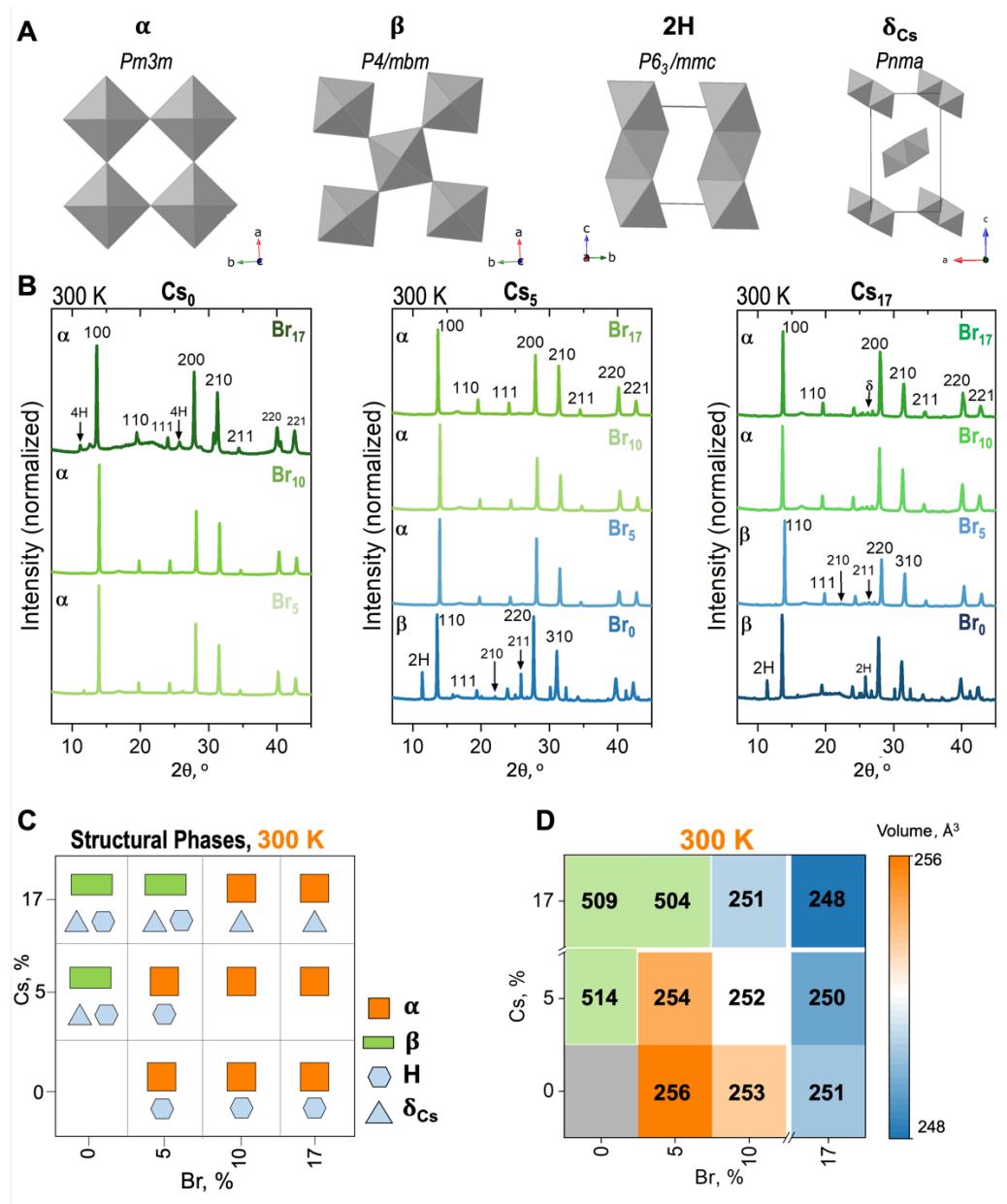


Figure 2. Crystal structure from powder XRD at 300 K. (A) Structural phases present in the $(\text{Cs},\text{FA})\text{Pb}(\text{I},\text{Br})_3$ set of compositions. (B) XRD patterns for different Cs-Br concentrations for the $(\text{Cs},\text{FA})-(\text{I},\text{Br})$ compositions at 300 K and vacuum, (C) Structural phases from Le Bail refinements, (D) Unit cell volume for the $(\text{Cs},\text{FA})-(\text{I},\text{Br})$ compositions at 300 K.

$(\text{Cs},\text{FA})\text{Pb}(\text{I},\text{Br})_3$ Temperature Phase Diagram

To compose a low-temperature phase diagram for the $(\text{Cs},\text{FA})-(\text{I},\text{Br})$ compositional space, we evaluated the *in-situ* XRD of all samples by cooling the powders from 300 K to 23 K in steps of 20 K (Figures S5-7). From a general phase analysis, by plotting the diffraction pattern as a function

of temperature (**Figure S8**), we identified the phase transition temperatures as new diffraction peaks appeared. These phase transition temperatures for all compositions are shown in **Table S2**. To show the overall mixed-cation and mixed-halide temperature phase diagram, we divided it into three, for three Cs molar precents, Cs_0 , Cs_5 , and Cs_{17} (**Figure 3**). Therefore, each temperature phase diagram is shown as a function of Br molar %.

First, **Figure 3A** shows the phase diagram for Cs_0Br_x . For Cs_0Br_0 and Cs_0Br_5 , there are two low-temperature phase transitions, from α to β slightly above 250 K, and from β to γ around 150 K. These two phase transitions have been reported for pure-iodide single-cation perovskites⁵⁻⁸, mixed-cation (Cs,FA),¹² and mixed-cation (MA,FA).^{11,30} Generally, it is expected for the perovskite to decrease its symmetry as it is cooled down, evidenced by the tilting of the corner-sharing octahedra from cubic to tetragonal and from tetragonal to orthorhombic. These transitions are also foreseen given that as the temperature decreases, the organic cations move slower and influence the octahedra tilting due to less movement. Moreover, when increasing the Br content to $\text{Cs}_0\text{Br}_{10}$ and $\text{Cs}_0\text{Br}_{17}$, we observe only one phase transition from α to β from 300 K to 20 K. This represents higher stability of the tetragonal phase without the transition to orthorhombic, meaning there is less tilting of the octahedra. According to Johnston and coworkers,³¹ Br incorporation, up to around 15%, suppresses cation rotation in mixed-halide perovskites at room temperature. Therefore, we can explain that the suppressed cation rotation at room temperature keeps constant down to low temperatures. With respect to secondary phases, without Cs into $\text{FAPb}(\text{I},\text{Br})_3$ (Cs_0Br_x) we observe the presence of hexagonal polytypes (H) in **Figure S9** (explained in the previous section at 300 K).

Figure 3B shows the temperature phase diagram for $\text{Cs}_{0.05}\text{FA}_{0.95}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ (Cs_5Br_x). For Cs_5Br_0 , we observe the β phase at 300 K. We observe one phase transition from β to γ at 150 K.

Adding Br, Cs_5Br_5 and $\text{Cs}_5\text{Br}_{17}$, leads to an initial α phase, indicating a higher perovskite symmetry at 300 K and discussed in the previous section of **Figure 2**. Cooling down the Cs_5Br_x perovskites leads to one phase transitions from α to β slightly above 250 K, similar to the Cs_0Br_x set. However, for all Cs_5Br_x compositions, adding Br hinders the transition from β to γ , indicating better stability of the tetragonal phase and a higher perovskite symmetry at low temperatures such as 23 K. In general, for Cs_5Br_x , no secondary phases are observed (**Figures S9-10**).

Figure 3C shows the temperature phase diagram for the case of $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ ($\text{Cs}_{17}\text{Br}_x$). Analogous to Cs_5Br_0 , without Br $\text{Cs}_{17}\text{Br}_0$, the mixed-cation perovskite adopts the tetragonal structure at 300 K. This composition shows a phase transition from β to γ at around 150 K. At 300 K, adding Br, $\text{Cs}_{17}\text{Br}_5$, retains the tetragonal perovskite structure. Remarkably, this composition shows no phase transitions in the studied range from 300 K to 23 K; the β perovskite phase is stable down to very low temperatures. Increasing the Br content ($\text{Cs}_{17}\text{Br}_{10}$, $\text{Cs}_{17}\text{Br}_{17}$) leads to an initial α perovskite phase that will then transform to β phase at around 270 K.

Equivalent to the $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ phase with Cs_5Br_x , for $\text{Cs}_{17}\text{Br}_x$, we observe that adding Br suppresses the phase transition from β to γ all the way down to 23 K. Therefore, adding Br improves the stability and increases the symmetry of the perovskite structure at very low temperatures. Regarding the secondary phases, all compositions with $\text{Cs}_{17}\text{Br}_x$ show a minor peak corresponding to the non-perovskite δ_{Cs} (**Figure S10**) due to phase segregation since it overpasses the solubility limit.¹² It is known that this non-perovskite is photoinactive and unwanted for solar cell applications.⁴

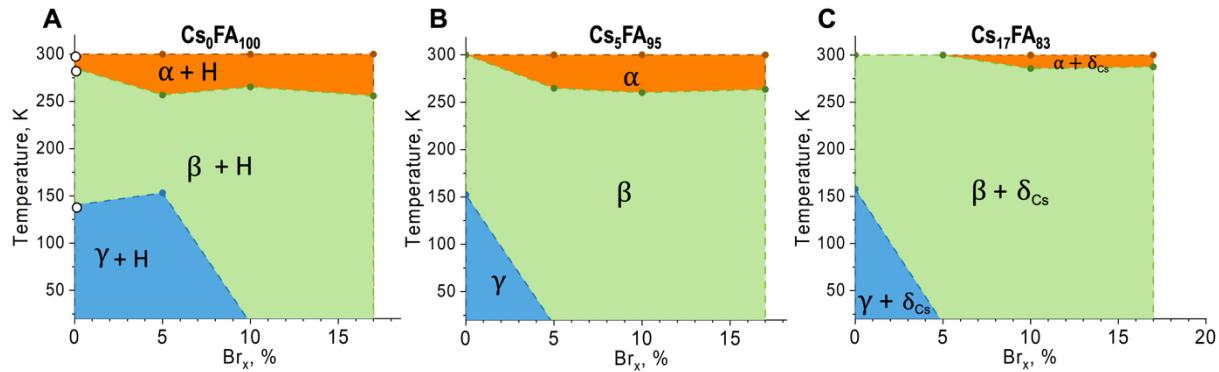


Figure 3. Composition – Temperature phase diagram. Mixed-halide mixed-cation lead halide perovskites in the $(\text{Cs},\text{FA})\text{Pb}(\text{I},\text{Br})_3$ compositional space. (A) without Cs (Cs_0Br_x) as a function of Br, (B) Cs 5% (Cs_5Br_x) as a function of Br, (C) Cs 17% ($\text{Cs}_{17}\text{Br}_x$) as a function of Br.

Br addition improves stability at low temperatures

We evaluated the low-temperature phase transitions for a mixed cation (Cs,FA) and mixed-halide (I,Br) perovskite, as shown in **Figure 1A**. In **Figure 3**, we presented the three phase diagrams to compare different ratios of mixed-cation (Cs,FA) and mixed-halide (I,Br). These phase diagrams reveal that the addition of Br to mixed-cation (Cs,FA) compositions stabilizes the perovskite β phase over a wide temperature range, from approximately 260 K down to 23 K. This stabilization prevents significant structural changes, symmetry variations, and octahedral tilting that occur in the γ phase.³² **Figure 4** illustrates the *in-situ* XRD pattern and results for two compositions, Cs_5Br_0 and $\text{Cs}_5\text{Br}_{17}$. The complete set of temperature-dependent diffraction patterns can be found in **Figures S5-8**. **Figures 4A-B** show two significant diffraction regions for the (A) $\text{Cs}_5\text{Br}_{10}$ and (B) $\text{Cs}_5\text{Br}_{17}$ powders as the samples are cooled down from 300 K (orange) to 23 K (blue). The main perovskite Bragg peaks are highlighted, and the Bragg peaks corresponding to non-perovskite 2H and δ_{Cs} phases are shown. **Figures 4C-D** show the diffraction regions from 21.5° to 27° as a function of temperature for (C) Cs_5Br_0 and (D) $\text{Cs}_5\text{Br}_{17}$. For Cs_5Br_0 in **Figure 4C**, the perovskite phase starts as β at 300 K, with characteristic peaks around 22° and 26.5° corresponding to the 210

and 211 Bragg peaks of the tetragonal phase. For Cs_5Br_0 , a new peak appears around 23.2° at 167 K, indicating the presence of the γ phase. In contrast, **Figure 4D** shows that for $\text{Cs}_5\text{Br}_{17}$, the perovskite phase initially adopts the α structure. As the temperature decreases, Bragg peaks of the β phase appear at ~ 267 K, and no peak related to the γ phase is observed down to 23 K. Furthermore, $\text{Cs}_5\text{Br}_{17}$ does not exhibit any diffraction peaks attributed to secondary phases, maintaining a single perovskite phase structure from 300 K to 23 K. For further analysis, from Le Bail refinements we obtained the unit cell's lattice parameters (Tables S3-S4, **Figures S11** and **S12**) and the unit cell volume (**Figures 4E-F**). **Figure 4E** shows the unit cell volume as a function of temperature for a composition without Br, Cs_5Br_0 . We observe a significant increase in volume from 300 K to 280 K. However, in both cases, it fits a tetragonal structure of the space group $P4/mbm$. After the initial increase, the volume decreases as temperature decreases, as expected.⁹ Below 160 K, the perovskite phase transforms into γ phase with space group $Pbnm$. Therefore, the unit cell volume increases and then keeps decreasing as a function of temperature. When adding Br ($\text{Cs}_5\text{Br}_{17}$), **Figure 4F** shows the unit cell volume as a function of temperature, evidencing the phase transition from α to β . For the β phase, there is a linear decrease of the unit cell volume as a function of temperature down to 23 K.

The observed phase transitions and structural behavior in mixed-cation mixed-halide perovskites differ from those reported in single-cation or single-halide systems. Adding Br to single-cation iodide compositions, such as $\text{MAPb}(\text{I},\text{Br})_3$ ⁹ or $\text{CsPb}(\text{I},\text{Br})_3$,¹⁰ has resulted in a transition from the β to the γ phase. Similarly, in mixed-cation and single-halide systems, such as $(\text{Cs},\text{FA})\text{PbI}_3$, the transition to the γ phase has been reported in the range of miscibility.⁵ Remarkably, in $(\text{Cs},\text{FA})\text{PbBr}_3$, Cs substitution has been shown to suppress phase transitions at lower temperatures.¹⁴ Motzur et al. attributed this phase stability to local compressive strain caused

by Cs substitution, overriding the orientation driven by the organic–organic interactions and disrupting changes in low-temperature phase transitions. They highlighted the sensitivity of organic–organic interactions in FAPbBr_3 , explaining the advantages of Cs incorporation in halide perovskites. Other studies have also reported the suppression of phase transitions by incorporating Cs in MAPbBr_3 , attributed to compressive chemical pressure.³² Similarly, Ray et al. suppressed the orthorhombic phase of MAPbBr_3 by adding DMA and forming a mixed-cation $(\text{MA},\text{DMA})\text{PbBr}_3$ perovskite.¹⁶ This suppression was attributed to increased disorder of organic cations and a less distorted inorganic framework.³³ Building upon this understanding, we suggest that the addition of Cs and Br to the FAPbI_3 perovskite, forming a $(\text{Cs},\text{FA})\text{Pb}(\text{I},\text{Br})_3$ framework compresses the structure, as evidenced by smaller lattice parameters, affecting the interactions between organic cations and increasing disorder.

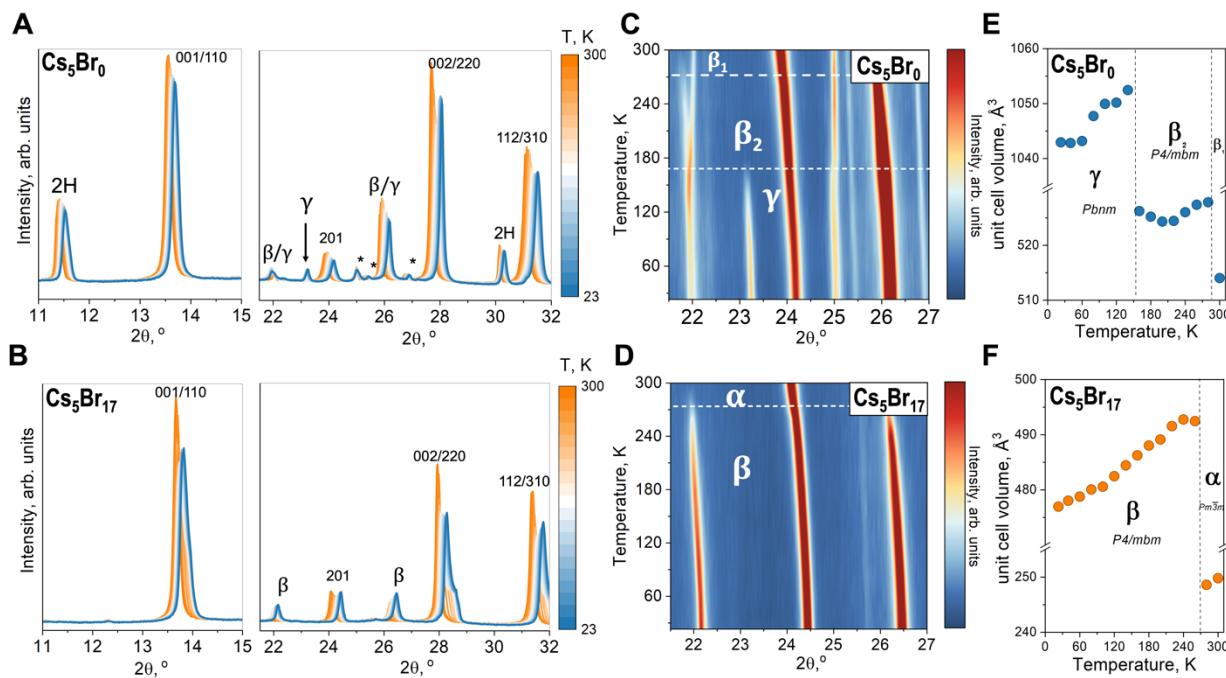


Figure 4. The effect of adding Br into the (Cs,FA)PbI₃ lead halide perovskites by *in-situ* X-ray diffraction in a Cs 5 % composition. (A,B) Diffraction patterns for all set of studied temperatures in two ranges of 2θ, from 11-15 ° and 21.5-32 ° (A) Cs₅Br₀ and (B) Cs₅Br₁₇. (C,D) Temperature versus diffraction plot from 21.5-27 ° for (C) Cs₅Br₀ and (D) Cs₅Br₁₇. (E,F) Unit cell volume as a function of temperature from Le Bail refinements for (E) Cs₅Br₀ and (F) Cs₅Br₁₇.

To evaluate the effect of crystal structure variations in the electrical properties of $(\text{Cs},\text{FA})\text{Pb}(\text{I},\text{Br})_3$ perovskites, we deposited perovskite thin films for 6 selected compositions and used them to fabricate and evaluate the performance of solar cells (**Figure S13**). In general, by analyzing the crystal structure of the perovskite films using room temperature XRD (**Figure S13A**), the thin film samples without Cs (Cs_0Br_x) or Cs_5Br_x did not show the same perovskite or non-perovskite phases as the powder samples (**Figure 2**). We attribute this inconsistency to different thin film deposition parameters, such as solvent and antisolvent, that play a critical role in the crystallization kinetics and phase formation of the metastable perovskite.³⁴ Non-perovskite hexagonal phases are detrimental to solar cell performance in FAPbI_3 -based compositions.^{35,36} Therefore, the composition that showed the minimum power conversion efficiency in solar cells was $\text{Cs}_0\text{Br}_{17}$ (**Figure S13B**), partially due to hexagonal secondary phases (**Figure S13A**). $\text{Cs}_5\text{Br}_{17}$ also showed a low-performance solar cell and the presence of non-perovskite phases. The best power conversion efficiency of solar cells was the composition $\text{Cs}_{17}\text{Br}_{10}$, correlated to a single-phase perovskite.

To evaluate the charge carrier transport properties, we chose two perovskite thin film compositions with the same crystal structure as their powder samples, one without Br ($\text{Cs}_{17}\text{Br}_0$) and $\text{Cs}_{17}\text{Br}_{17}$ (**Figure S14**). We used time-resolved THz spectroscopy to measure the charge carrier mobility as a function of temperature for $\text{Cs}_{17}\text{Br}_0$ and $\text{Cs}_{17}\text{Br}_{17}$, as shown in **Figure 5** (methods in the SI). Consistent with literature reports where higher Br content leads to lower carrier mobility, the carrier mobility for $\text{Cs}_{17}\text{Br}_{17}$ is lower than that for $\text{Cs}_{17}\text{Br}_0$ at all temperatures.^{3,37} We observe that the carrier mobility increases for both compositions as the temperature decreased from 300 K to 100 K. The increase in carrier mobility is expected given that lower phonon vibrations at lower temperatures improve carrier transport.³⁸ We observe a small discontinuity in the mobility data, in

contrast to other reports where no significant discontinuities across structural phase transitions were observed.³⁸ For the film without Br ($\text{Cs}_{17}\text{Br}_0$) in **Figure 5A**, we observe a slope change corresponding to a phase transition at around 175 K, which we attribute crystal phase transition from β to γ , close to the powder phase transition temperature in **Figure 3C** and **Figure S8**. Similarly, when adding Br ($\text{Cs}_{17}\text{Br}_{17}$), **Figure 5B** shows the phase transition from α to β at around 270 K, close to the phase transition observed by in-situ XRD (**Figure 3C**, **Figure S8**). The increase in mobility for both samples at lower temperatures is modest because we average the mobility values across different excited carrier densities (**Figures S15** and **S16**). At higher excitation fluences, carrier-carrier scattering dominates the carrier mobility rather than phonon scattering. By examining the average carrier mobility at both high and low excitation fluences, the impact on carrier transport due to the structural phase transition is visible and not masked by temperature-dependent phonon scattering.³⁹ Overall, the carrier mobilities of the two samples across the temperature range probed are very similar, supporting that the crystal symmetry is not the dominant factor in determining carrier transport in perovskite materials.³⁹

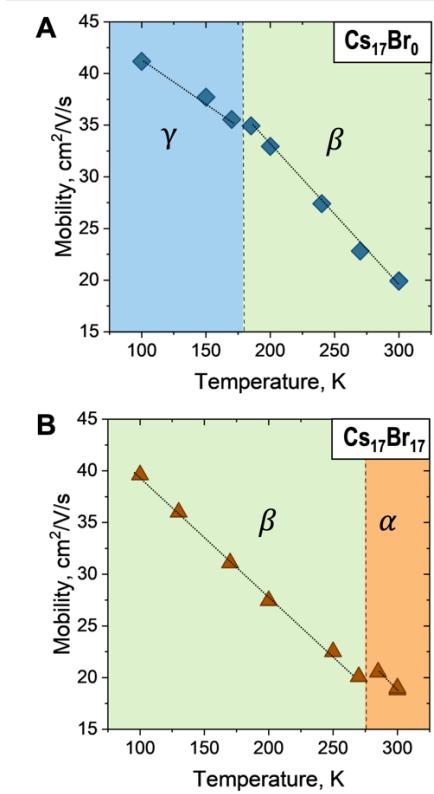


Figure 5. Carrier mobility as a function of temperature. (A) without Br $\text{Cs}_{17}\text{Br}_0$, and (B) with Br $\text{Cs}_{17}\text{Br}_{17}$. The lines are to guide the eye and highlight discontinuity across phase transition temperatures.

Conclusions

In conclusion, this work shows for the first time the low- temperature phase transitions for a mixed-cation and mixed-halide perovskite. We measured *in-situ* powder XRD to create temperature phase diagrams for different concentrations of Cs and Br in $(\text{Cs},\text{FA})\text{Pb}(\text{I},\text{Br})_3$ perovskites. By replacing I with Br in (Cs,FA) compositions, we found that the transition from a tetragonal to orthorhombic phase at low temperatures (below 150 K) was suppressed, resulting in a more symmetrical perovskite structure with potential applications at low-temperature settings. When Cs was not present, we observed the formation of non-perovskite hexagonal phases. However, the addition of Cs and Br prevented the formation of the hexagonal structures. It is important to note that the

inclusion of 17 % Cs resulted in the formation of the secondary non-perovskite orthorhombic δ -CsPbI₃ phase. From these findings, it can be concluded that adding Br to (Cs,FA) perovskites enhances the stability of the β phase over a wider temperature range, which is advantageous for low-temperature applications. Although the introduction of Br increases the bandgap of the perovskite, which reduces the number of absorbed photons, the overall crystal structure becomes more robust and contributes to long-term stability. To gain a comprehensive understanding of how the crystal structure behaves across the entire temperature range, further investigations focusing on the fundamental structural aspects are essential.

Author Contributions

J.H wrote the manuscript, synthesized all powder samples, characterized powder XRD, UV-Vis, did all the LeBail refinements, fabricated the solar cells, and analyzed all data. All powder samples were synthesized and characterized at HZB, under the supervision, guidance, and help in the analysis from J.B and S.S. D.T helped in the *in-situ* XRD experiments at BESSY II and contributed to data analysis. D.K.L fabricated and measured XRD and analyzed all thin films. C.N.B measured THz under the supervision and analysis of M.J.S. J.P.C.B and S.S supervised the entire work. All the authors have read, corrected, and agreed with the manuscript.

Acknowledgements

All authors thank the Helmholtz-Zentrum Berlin für Materialien und Energie for the allocation of synchrotron radiation beamtime at the KMC-II Diffraction beamline at BESSY II (ST- 221-11048). J.H acknowledges the DAAD German Academic Exchange one year grant for career and the Graduate Education for Minorities (GEM) fellowship for the complete year project funding.

D.K.L acknowledges the NSF-GRF DGE-2039655 funding. M.J.S and C.N.B acknowledge the NSF DMR 2316827 funding. Any findings and conclusions are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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