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Mixed A-Cation Perovskites for Solar Cells: Atomic-Scale Insights Into Structural Distortion, Hydrogen Bonding and Electronic Properties

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Abstract

Hybrid lead halide perovskites containing a mixture of A-site cations such as the formamidinium ($\text{CH}(\text{NH}_2)_2^+$, FA) and the smaller caesium (Cs^+) cations have attracted considerable interest due to their improved stability and solar cell performance. However, the structural changes at the atomic-scale and modifications to the optoelectronic properties of these mixed cation perovskites are not fully understood. Here, we investigate the $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ ($x \leq 0.25$) system using a combination of static and dynamic *ab initio* computational methods. We find that the incorporation of Cs^+ cations into the parent FAPbI_3 structure induces a chemical pressure or lattice strain effect through Cs/FA ion size mismatch resulting in structural distortion and stronger FA-iodide (N-H \cdots I) hydrogen bonding interactions. The dynamic tilting of PbI_6 octahedra and the rotational motion of FA cations are also suppressed, which leads to symmetry-breaking

of the lattice. Such symmetry-breaking distortions of the Pb/I lattice give rise to a Rashba-type effect, which spin-splits the frontier electronic bands making the band gap indirect. Our results suggest that the direct-indirect band gap transition may be a factor in the reduced charge-carrier recombination rate in these mixed cation perovskites.

1. Introduction

Lead halide perovskite solar cells have shown a remarkable rise in power conversion efficiency from 3.8% to over 22% in less than a decade.¹⁻⁹ Along with their solution-processed fabrication, they possess many suitable properties for solar absorbers, including long charge carrier lifetimes, a tunable band gap by cation or halide substitution and compatibility with a wide range of charge collecting layers.

Despite their promising properties, a number of challenges need to be overcome before perovskite-based solar cell devices can be commercialised. Long-term stability at ambient conditions is one of the most important issues.¹⁰⁻¹⁴ Compositional engineering has recently emerged as a potential approach to deliver higher stability without sacrificing power efficiency.¹⁵⁻³² Lead halide perovskites typically have the composition APbX_3 with the A-site occupied by a monovalent organic or inorganic cation (e.g. methylammonium CH_3NH_3^+ (MA^+), formamidinium $\text{CH}(\text{NH}_2)_2^+$ (FA^+) or caesium Cs^+) and the X-site by a halide anion (I^- , Br^- or Cl^-). The PbX_3 component forms a framework cage of corner-sharing octahedra (shown in Figure 1) with the A-site cation (termed A-cation hereafter) at the centre of each cage. Among compositional engineering approaches, mixing of different sized A-cations has shown promise in producing longer lived solar cells.^{17-22,24-28,33} In particular, partial substitution (of up to 25 %) of FA cations by the much smaller Cs cations in FAPbI_3 stabilizes the perovskite phase against phase transitions and chemical degradation.^{18,20,21,28,33,34} These mixed FA/Cs perovskites also exhibit improved optoelectronic properties, such as a tuned band gap,¹⁸ enhanced charge-carrier mobility²⁰ and recombination lifetime,²⁰ and reduced energetic disordering.¹⁸ As the static and dynamical structures influence these properties,

it has been suggested that A-cation mixing modifies the internal interactions between the octahedral inorganic framework and organic cations. Despite a number of experimental reports and intriguing proposals, an in-depth atomistic understanding of these improvements is currently unclear.

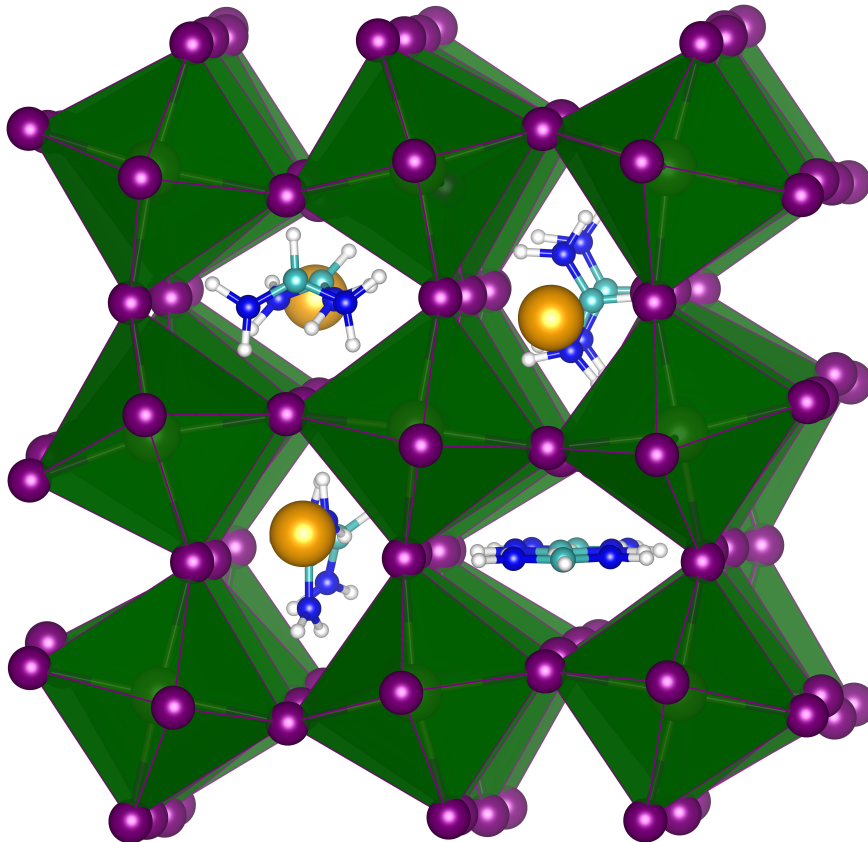


Figure 1: Schematic structure of a mixed A-cation metal halide perovskite. The A cations, FA^+ and Cs^+ , occupy the inorganic cavity formed by corner-sharing PbI_6 octahedra (green). Key: iodine (purple), hydrogen (white), carbon (cyan), nitrogen (blue), caesium (orange).

We have carried out a range of recent studies on hybrid halide perovskites including work on ion transport, degradation and defect passivation.^{14,35-42} Here, we extend our previous work by investigating the structural distortions and interatomic interactions between the organic cations and inorganic framework of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ ($x \leq 0.25$). Insights into the atomic-scale dynamical processes of the PbI framework and the organic cations are also provided by *ab initio* molecular dynamics simulations. The impact of A-cation mixing on the photovoltaic behaviour and possible Rashba-type effects has been investigated by exploring

electronic properties of these perovskites.

2. Methods

Ab initio simulations were performed within the framework of density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP)^{43,44} using the Perdew-Burke-Ernzerhof functional for solids (PBEsol) within the Generalised Gradient Approximation (GGA).^{45,46} The projected augmented wave (PAW)⁴⁷ method and a plane-wave cutoff energy of 500 eV were employed for all the calculations. To simulate the impact of Cs incorporation with experimental concentrations of up to 25%,^{20,33} a sufficiently large $4\times 4\times 4$ supercell (64 A-cations) of the parent FAPbI₃ was chosen. We stress the necessity of a large structural supercell to model the experimental compositions for mixed A-cations. The extensive configuration space of cation distributions further makes the *ab initio* computational investigations extremely challenging. Geometry relaxation was performed with k -point sampling at the Γ point and the interatomic forces were relaxed with the convergence criteria of 0.01 eV \AA^{-1} . A $3\times 3\times 3$ Γ -centred Monkhorst-Pack sampling mesh with a Gaussian smearing of 0.01 eV was used for the electronic structure evaluation. To introduce a spin-orbit coupling (SOC) correction, geometry optimized $2\times 2\times 2$ supercells of selective systems were considered. A $5\times 5\times 5$ Γ -centred mesh was considered for the SOC-corrected electronic structure calculations.

To consider various possible conformations of FA⁺ cations in FAPbI₃, the structural optimizations were initiated from up to 40 randomly generated geometries. We find that different orientations of the FA⁺ cations result in small changes in total ground-state energy and lattice parameters. By exploring the configurational space for the mixed A-cation system FA_{0.85}Cs_{0.15}PbI₃, the highly dispersed Cs cation arrangements produced the lowest energy geometries and such a cation distribution has been considered in this study (see Supporting Information (SI) for further details).

To investigate finite temperature effects, we also performed *ab initio* molecular dynamics simulations at 300 K using the CP2K package.⁴⁸ The QUICKSTEP formalism,⁴⁹ analytical dual-space pseudopotentials,⁵⁰ the GGA of the PBEsol form and dispersion corrections as prescribed by Grimme (DFT-D3)⁵¹ were used. Equilibrium dynamics were maintained in the NPT ensemble using a Nose-Hoover thermostat and a barostat as formulated by Martyna *et al.*⁵² With a timestep of 1 fs, each simulation covered a period of 40 ps, with the equilibration spanning the first 5 ps.

3. Results and Discussion

3.1 Structural Distortion of the Perovskite Lattice

Simulations of the perovskite structures indicate that the lattice volume of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ ($x \leq 0.25$) reduces with increasing Cs^+ content (Fig. 2a), which is in agreement with X-ray diffraction studies.^{21,33} The reduction of the unit cell volume in these mixed A-cation perovskites indicates chemical pressure effects, which relate to the internal structural contraction induced by the ion size mismatch between FA^+ (2.53 Å) and much smaller Cs^+ (1.67 Å).⁵³ Due to the soft mechanical nature of hybrid perovskites (with a bulk modulus <18 GPa^{54,55}), such effects can be tuned by mixing the large and small sized A-cations in controlled proportions. These structural perturbations are expected to have prominent effects on their phase transitions,⁵⁶ solubility of ions in solid solutions,¹⁸ and optoelectronic properties.⁵⁴

By substituting small sized Cs^+ cations in place of FA^+ , the parent cubic lattice contracts anisotropically and lowers the crystal symmetry to a tetragonal phase. The a and b lattice parameters contract whereas the c lattice parameter elongates, increasing the c/a ratio by 2.8% (Fig. 2b). This structural change leads to symmetry-reducing tetragonal distortion in the $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ lattice upon A-cation mixing. The main source of the anisotropic volume contraction could be either the reduced internal volume of the PbI_6 octahedra with

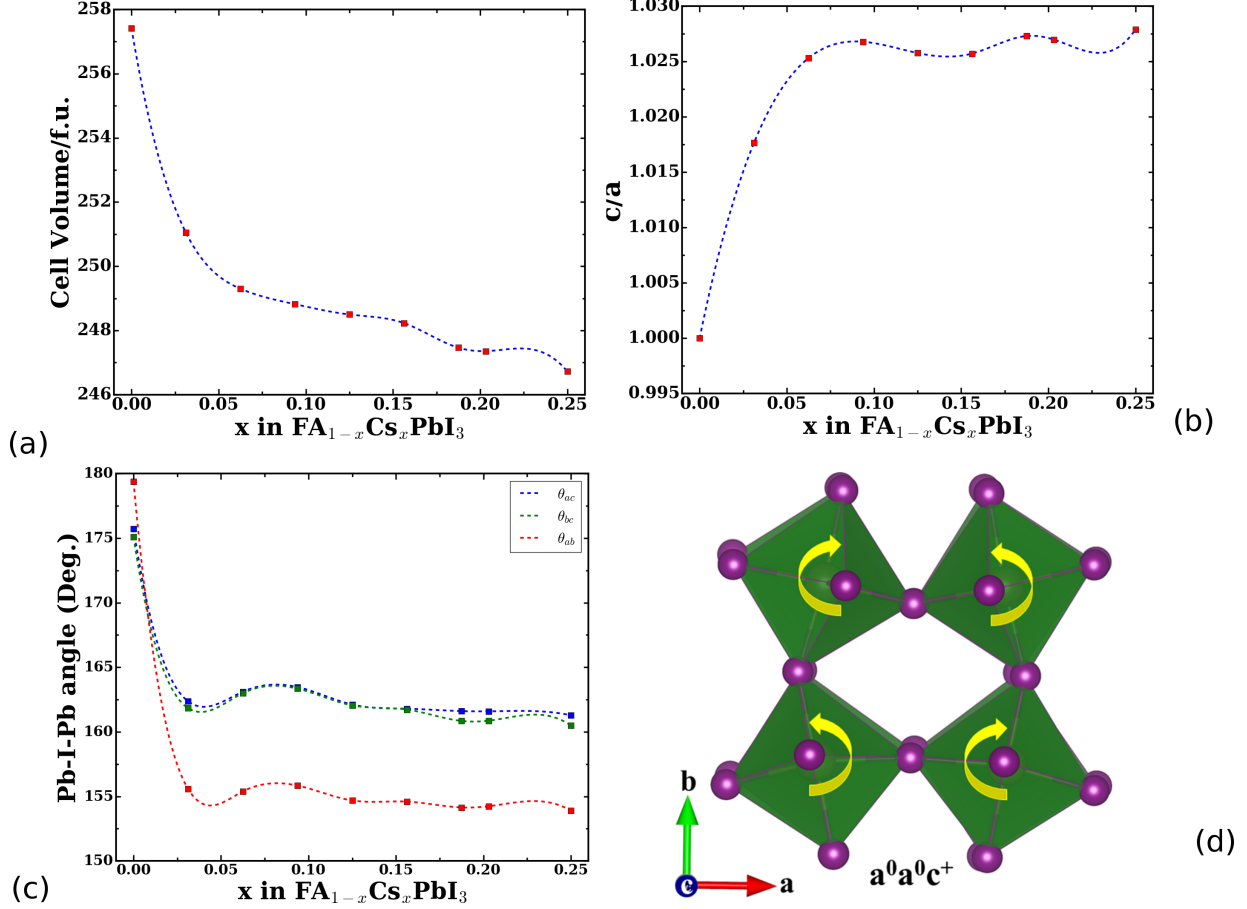


Figure 2: Structural distortion in $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$. (a) Cell volume per formula unit, (b) c/a ratio and (c) average Pb-I-Pb angle in three planes. (d) Tilting of PbI_6 octahedra with mutual in-phase rotation i.e. $a^0a^0c^+$ in Glazer's notation for $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$. Yellow arrows indicate the direction of rigid rotation of octahedra.

compressed Pb-I bonds and/or the octahedral tilting of corner-sharing PbI_6 . To investigate both possibilities, we analyse (1) the average PbI_6 octahedral volume and the Pb-I bond distances, which indicate the distortion inside the octahedra, and (2) Pb-I-Pb angles, which represent the magnitude of the octahedral tilting. We find that the average PbI_6 volume and Pb-I bond lengths (Fig. S3 a,b) remain unchanged upon A-cation mixing. Thus, A-cation mixing keeps the internal structure of PbI_6 octahedra unaltered. Interestingly, this contrasts with the tin-based system $\text{FA}_{1-x}\text{Cs}_x\text{SnI}_3$, where the Sn-I bond contracts with Cs^+ incorporation.³³

Our results indicate that the average Pb-I-Pb angles decrease along with the lattice

contraction of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ (shown in Fig. 2c). Specifically, with increasing Cs^+ concentration, the Pb-I-Pb bond angles are more strongly reduced in the ab -plane (θ_{ab}) than in the other planes (θ_{bc} and θ_{ac}), indicating rotation of PbI_6 octahedra about the c -axis. As shown in Fig. 2d, adjacent PbI_6 octahedra tilt in the same direction, that is, ‘in-phase’ about the c -axis.³³ Using Glazer notation,⁵⁷ such one-tilt rotations of octahedra are denoted $a^0a^0c^+$.

Therefore, as a consequence of the FA/Cs ion size mismatch, the cell volume contracts by tilting the PbI_6 octahedra. In a similar manner, applying low hydrostatic pressure (< 5 GPa) has also been found to induce similar octahedral tilting based distortions and phase transitions in other hybrid perovskites including MAPbI_3 and FAPbI_3 .^{58–60} Tilting of corner-sharing octahedra is a relatively low-energy process^{58,59,61} in these hybrid lead perovskites and consequently it becomes the source of structural distortion under weak perturbations such as cation substitution and mild external pressure.

3.2 Effect of H-bonding

Lattice distortions can also modify the hydrogen bonding interactions between FA^+ cations and the PbI framework as discussed in our previous study.³⁶ By analysing the $\text{H}_N \cdots \text{I}$ bonds in FAPbI_3 , we find the shortest distances are 2.75 and 2.95 Å (see Fig. 3a). In contrast, on incorporation of Cs, as in $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$, all four $\text{H}_N \cdots \text{I}$ hydrogen bonds become much stronger due to the structural distortions (Fig. 3b). As shown in Fig. 3b, all the $\text{H}_N \cdots \text{I}$ distances are now ~ 2.65 Å, which are shorter than that in the parent FAPbI_3 .

To evaluate the strength of hydrogen bonding in $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$, we perform an analysis based on the non-covalent interactions (NCI) index formulated by Johnson *et al.*^{62,63} This analysis uses the electron density and its spatial derivatives to identify the non-covalent bonds in materials including the hybrid perovskites.^{64,65} We analyse the reduced electron density gradient, s , as a function of $\text{Sign}(\lambda_2)\rho$, where ρ and λ_2 are respectively, the electron density and the second eigenvalue of the electron density Hessian (second derivative) matrix, respectively (Fig. 3c,d).⁶³ From this analysis, the appearance of troughs and singularities in

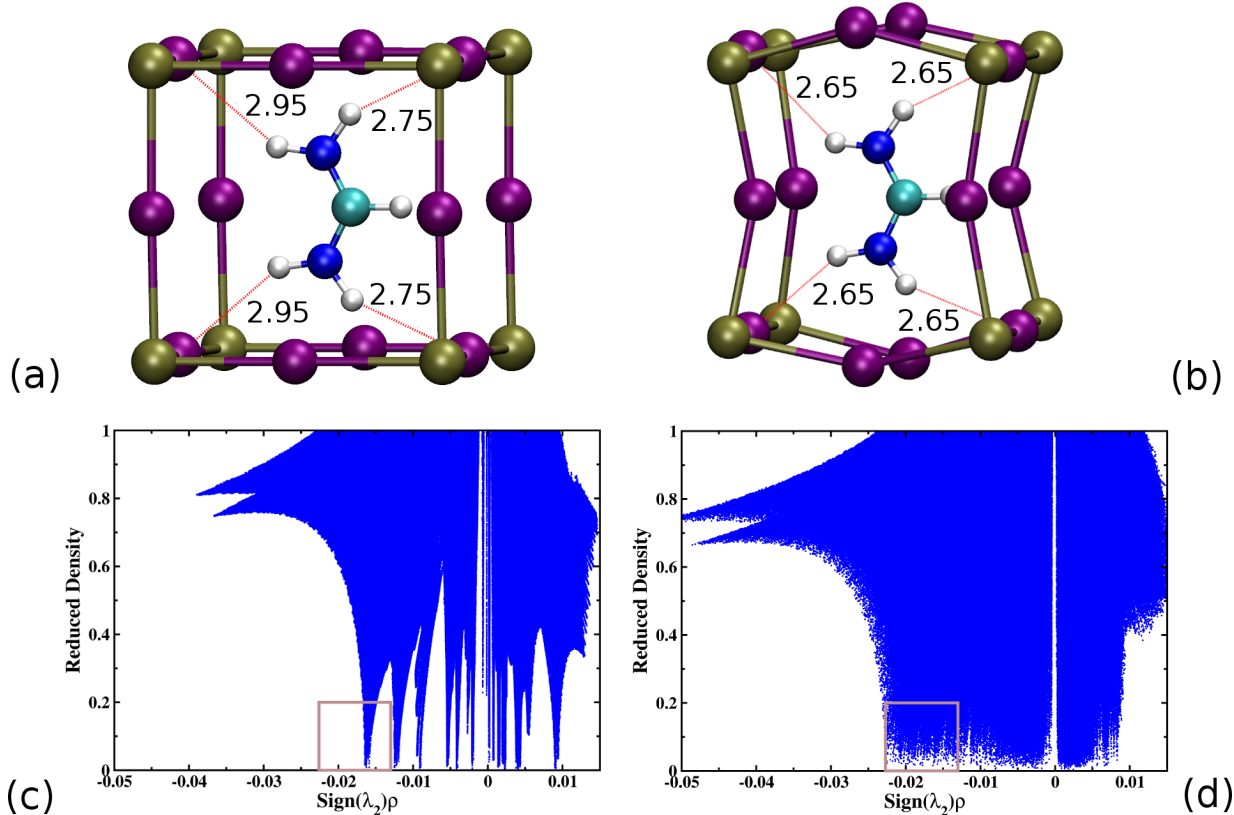


Figure 3: Enhanced hydrogen bonding with A-cation mixing. Schematic structures of $H_N \cdots I$ hydrogen bonds (red dashed lines) in (a) $FAPbI_3$ and (b) $FA_{0.85}Cs_{0.15}PbI_3$ with average bond lengths in Angstrom. Reduced density gradient (s) plot as a function of $Sign(\lambda_2)\rho$ for (c) $FAPbI_3$ and (d) $FA_{0.85}Cs_{0.15}PbI_3$. The brown boxes denote the range $-0.022 < \rho < -0.012$ where the hydrogen bonding mediated troughs are markedly different between $FAPbI_3$ and $FA_{0.85}Cs_{0.15}PbI_3$.

$s(\rho)$ indicate the presence of non-covalent interactions. The sign of λ_2 denotes the type of interaction: for $\lambda_2 < 0$, the interaction is attractive (such as hydrogen bonding), whereas in case of $\lambda_2 > 0$ it is repulsive (steric crowding). The interaction strength is determined by the density ρ ; the higher the absolute value of ρ the stronger the interaction.

As shown in Figure 3c,d a greater number of troughs appear in the range $-0.022 < \rho < -0.012$ for $FA_{0.85}Cs_{0.15}PbI_3$ than for $FAPbI_3$. The troughs also move to a higher negative value of ρ in the mixed A-cation lattice (Figure 3c,d). As the highlighted range of ρ in Fig. 3c,d indicates the degree of hydrogen bonding,⁶³ these plots show a strengthening of this non-covalent bonding interaction in the mixed A-cation perovskite. Due to the structural

distortion, H_N atoms of the FA cations become spatially constrained and closer to the iodide anions, enhancing the strength of $H_N \cdots I$ hydrogen bonding interactions.

The stronger hydrogen bonding between molecular cations and the Pb/I lattice increases the internal energy of the perovskite phase. This is confirmed by the calculation of a favourable Helmholtz free energy of mixing for $FA_{0.85}Cs_{0.15}PbI_3$ of the order of 92 meV/formula unit at 300 K. In addition, we have examined the enthalpy of decomposition of both $FAPbI_3$ and $FA_{0.85}Cs_{0.15}PbI_3$ to PbI_2 , FAI and CsI, and derived an exothermic value of -20 meV/formula unit and endothermic value of 135 meV/formula unit, respectively. We also find much weaker hydrogen bonding in the non-perovskite hexagonal phase of $FAPbI_3$ due to long $H_N \cdots I$ distances, with no significant change in hexagonal $FA_{1-x}Cs_xPbI_3$. This, in turn, correlates with the experimentally observed enhanced stability of the perovskite phase against the hexagonal phase for these mixed-cation halide perovskites.^{18,24,66}(see SI for details).

Hence, increased hydrogen bond strength helps to stabilize the structure and contributes to the greater thermal stability of the mixed A-cation perovskites. Similar phase stability induced by hydrogen bonding has also been observed for the low-temperature orthorhombic structure of $MAPbI_3$.^{11,67-70} From computational work on $MAPbI_3$, Bristowe and Cheetham⁶⁴ suggest that tuning the degree of hydrogen bonding can also be used as an additional control parameter to optimize perovskite solar cell properties.

3.3 Dynamics of Inorganic Framework and Molecular A-cations

A-cation mixing also affects the dynamic interactions and motion of the inorganic Pb/I cage and the organic cations.^{36,71} We therefore performed *ab initio* molecular dynamics simulations of the parent $FAPbI_3$ and mixed A-cation system $FA_{0.85}Cs_{0.15}PbI_3$ at 300 K. First, considering the inorganic framework, we plot two-dimensional (2D) volumetric maps of a representative PbI frame in the *ab*-plane (Fig. 4 (a,b)). The 2D volumetric map represents the probability of atoms occupying positions in space over the timescale of the simulation.

In Fig. 4a, the iodine atoms of the parent FAPbI_3 show a symmetric distribution around the lattice sites, which are iodine lattice sites of the high-symmetry cubic structure. Thus, the time-averaged trajectories demonstrate an almost perfect cubic phase of FAPbI_3 (Fig. 4a). In contrast, the 2D volumetric map for $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ (Fig. 4b) shows significant spatial distribution of iodine atoms away from the cubic lattice sites. The time-averaged structure consequently clearly indicates the distorted low-symmetry lattice for $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$.

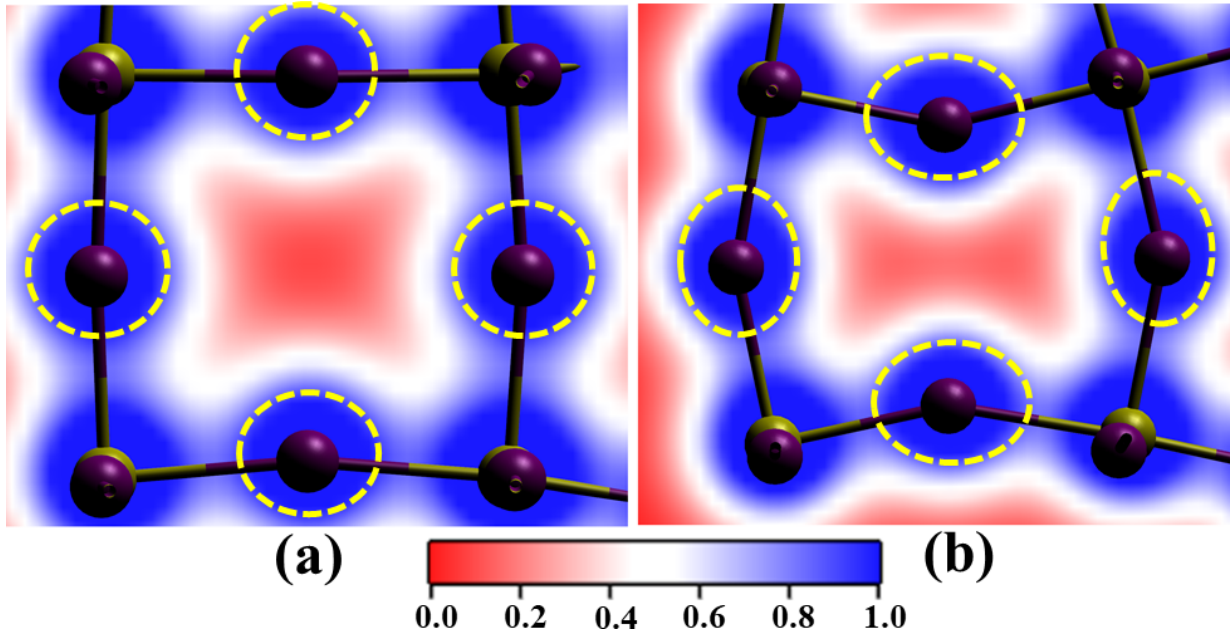


Figure 4: Dynamics of the inorganic framework in parent and mixed-cation perovskites. The volumetric plots of I and Pb atoms in a representative PbI -plane of (a) FAPbI_3 and (b) $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$. This plot represents the number density of atoms in space over simulation time. The scale is in arbitrary units, with blue and red indicating high and low number density, respectively. The ball-stick model of the inorganic framework shows the time-averaged positions of Pb and I atoms. The yellow dashed circles/ovals highlight the positions of iodine atoms over the simulation.

At room temperature, the iodide anions in FAPbI_3 oscillate about equilibrium positions in a regular cubic lattice with maximum displacements inside and outside of a cage due to periodic rotation of the octahedra about the pseudo-cubic axis.³⁶ As reported in recent high energy resolution inelastic X-ray scattering experiments and DFT-based computations, the energy barrier for octahedral tilting is only few meV in these mechanically soft perovskites and consequently, these oscillations are thermally active at room temperature.⁶¹ However,

our work shows that in $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ the iodide ions become constrained and oscillate through a smaller angle, with respect to their equilibrium positions either outside or inside of a PbI_6 cage, suppressing low-energy vibrational modes. This constraining of the lattice inhibits the periodic rotational motion of PbI_6 octahedra about the c -axis at 300 K, locking the octahedra across the whole structure in a tilted geometry. The suppressed octahedral tilting motion in $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ causes a static octahedral distortion, which has recently been identified by X-ray diffraction studies of Prasanna *et al.*³³

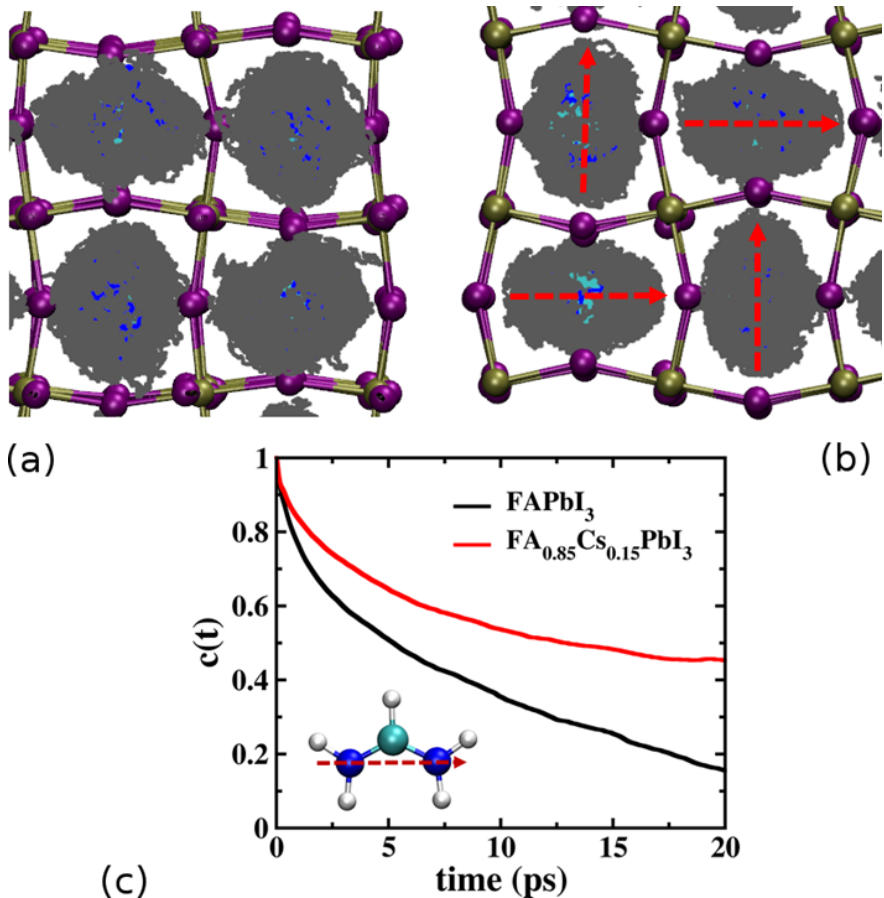


Figure 5: Dynamics of the FA^+ cation in parent and mixed-cation perovskites. The distribution of FA^+ cation in (a) FAPbI_3 and (b) $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ over simulation time. The ball-stick model of the inorganic framework is averaged position of Pb and I atoms over that time scale. Key: hydrogen (grey), carbon (cyan), nitrogen (blue). (c) Vector autocorrelation function of FA^+ cation exhibiting the probability of the cation remaining in its initial orientation over time. The molecular vectors of FA^+ ion in (b) and inset of (c) has been represented by red dashed arrows.

The molecular FA^+ cations also change their dynamic behaviour upon Cs^+ incorpora-

tion. As illustrated in Fig. 5a, the mobile FA cations in the parent FAPbI_3 explore full conformational space inside the inorganic cage showing no preferential orientation during the molecular dynamics simulation at 300 K. This disordered cation dynamics are in excellent agreement with quasi-elastic neutron scattering experiments, which also find a low barrier for reorientational motion inside the cage.^{12,72} In contrast, for $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$, the FA^+ cations exhibit constrained reorientational dynamics in which the N-N molecular axis preferentially align along the high-symmetry directions, [100] and [010] (Fig. 5b). Furthermore, neighbouring FA cations in the *ab*-crystal plane remain mutually perpendicular, orienting themselves along the elongated direction of the distorted cages (Fig. 5b and Fig. S4). Thus, the ordering of FA^+ cations is clearly influenced by the tetragonal distortion caused by the symmetry-lowering tilting of PbI_6 octahedra.

To further analyse the rotational motion of the FA^+ cations, we focus on the reorientation of the N-N molecular axis of the $\text{CH}(\text{NH}_2)_2^+$ cation (inset of Fig. 5c), to capture the tumbling or ‘jump-like’ rotation.⁷³ To obtain a quantitative description of this motion, we evaluate the vector autocorrelation function $c(t)$ of the N-N molecular axis from equilibrium trajectories. This function calculates the probability that the orientation of FA^+ cations remains directionally self-correlated over time. The faster the rotational correlation is lost, the faster the $c(t)$ decays with time.

As shown in Fig. 5c, the autocorrelation function for tumbling rotation of FA^+ cations in FAPbI_3 decays much faster than that of $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$. Notably, due to cation-lattice interactions, the FA^+ shows heterogeneous behaviour in their dynamics in which the organic cation is inside the inorganic cage. We have therefore employed a stretched exponential fit to these autocorrelation functions to calculate the rotational relaxation time (see SI for details). We derive relaxation times for FA^+ reorientation of 8.8 ps and 28.2 ps (with exponent values $\beta = 0.64$ and 0.48) in FAPbI_3 and $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$, respectively. The significant difference in relaxation times clearly indicate the restricted rotational dynamics of FA^+ cations at ambient conditions upon Cs^+ incorporation. Our simulated rotational relaxation time for

FA⁺ cations in FAPbI₃ matches well with a recent solid-state NMR study of Fabini *et al.*⁷⁴

In summary, the lattice contraction and tetragonal distortion of the inorganic framework causes the spatial confinement of FA⁺ cations, reducing the molecular tumbling dynamics at 300 K. Such restrained dynamics further increases the probability of the H_N atoms of CH(NH₂)₂⁺ to reside nearer to the electronegative iodide anions, enhancing the lattice-molecule interactions through stronger N-H···I hydrogen-bonding.³⁶ Since these effects reinforce each other, the reorientational modes of cation dynamics become restricted, causing partial immobilisation of FA cations along [100] or [010] crystal axes at room temperature. Recently, the suppression of cation dynamics and formation of an orientational glassy phase have been observed by neutron scattering studies of MA_{1-x}Cs_xPbBr₃ perovskites.⁷¹

3.4 Effect On Electronic Properties

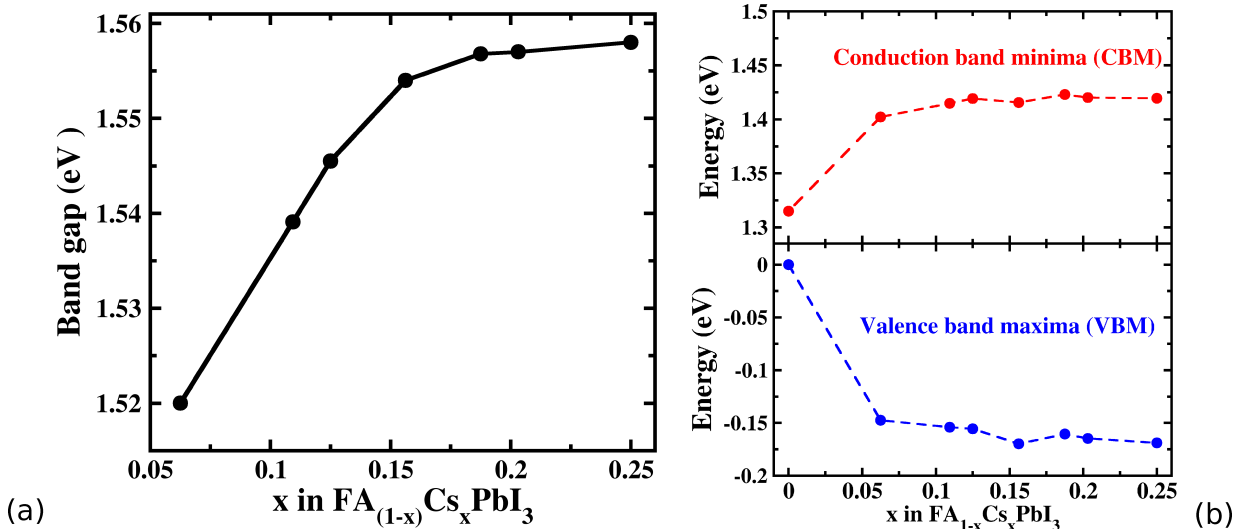


Figure 6: Electronic properties of FA_{1-x}Cs_xPbI₃ versus Cs concentration (x). (a) Change in band gap. (b) Variation in energy of conduction band minima (upper panel) and valence band maxima (lower panel). All the energies are scaled to VBM of FAPbI₃.

We now consider the electronic properties of FA_{1-x}Cs_xPbI₃ in relation to its photovoltaic behaviour. As shown in Fig. 6a, the band gap exhibits a blue-shift with increased Cs content from 1.52 eV (x = 0.06) to 1.59 eV (x = 0.25). Inclusion of spin-orbital coupling in the simulations, strongly underestimates the band gap of FA_{1-x}Cs_xPbI₃ (Table S1) although

the trend of variation with Cs concentration remains unchanged. This variation and increase are in agreement with recent experimental absorption studies.^{18,21,33} We note that due to the use of the semi-local exchange-correlation functional (PBEsol) the absolute band gap values have not been captured fully. The requirement for large simulation cell sizes prohibits us from applying a quasi-particle self-consistent GW approach with spin-orbit coupling corrections.⁷⁵ Nevertheless, as demonstrated in earlier studies,^{76,77} we can still analyze the key trends in electronic properties and the impact of A-cation composition.

Along with the band gap, the relative energies and chemical bonding character of the band edges directly affect charge separation, influencing their efficiency as perovskite solar cell devices.^{78,79} Applying the band-alignment scheme (see SI for details), the valence band maxima (VBM) downshifts in energy by 170 meV with increased Cs concentration, as shown in Fig 6(b). At the same time, the conduction band minima (CBM) shifts upward in energy by a smaller amount of 100 meV. Overall, this leads to a blue-shift in the band gap, which is consistent with experimental absorption studies.³³ Note that inclusion of spin-orbit coupling does not change the overall trend in shifts of the band edges. We recognize that models based on band alignment have approximations. Nevertheless, the change in the band edges can tune the band offset between perovskite and charge transport layers, which may facilitate charge-carrier separation and transfer.⁷⁹

To investigate the atomistic origin of the shift in energy level positions, we performed a detailed investigation of the chemical bonding nature of the CBM (Fig. 7a,b) and VBM (Fig. 7c,d). The charge density contours in Fig. 7c,d show that the VBM originates from the antibonding overlap of Pb 6s and I 5p* orbitals, consistent with previous reports.^{76,77} Furthermore, the site-projected density of states (pDOS, see Fig. S5) indicate the covalent bonding nature of the VBM, in which 6s orbitals of Pb and 5p orbitals of I contribute $\sim 30\text{-}35\%$ and $\sim 65\text{-}70\%$, respectively. For cubic FAPbI₃, where the Pb-I-Pb alignment is almost linear, the antibonding orbital overlap in the VBM state remains significant (Fig. 7c). With A-cation mixing, the in-phase PbI₆ octahedral tilting causes symmetry-lowering

lattice distortion where the Pb-I-Pb bond angles deviate from 180° , so that the I atoms are displaced out of the linear bonding geometry (see Fig. 7d). This distortion reduces the energetically unfavourable antibonding overlap between Pb 6s and I 5p* orbitals, causing a decrease in the energy of the VBM of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$. Similar modification of the VBM across the structural phase transition of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ has been reported from experimental spectroscopy studies.³³

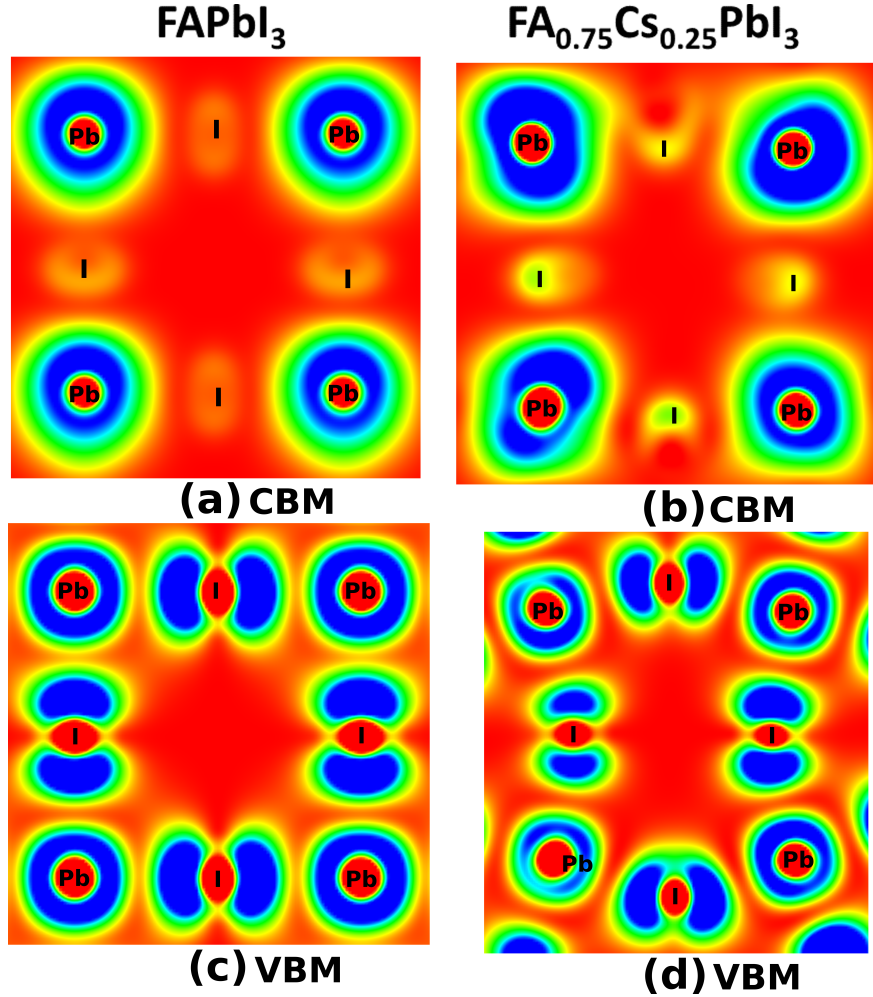


Figure 7: Electronic charge density contours. The CBM of (a) FAPbI_3 and (b) $\text{FA}_{0.75}\text{Cs}_{0.25}\text{PbI}_3$. The VBM of (c) FAPbI_3 and (d) $\text{FA}_{0.75}\text{Cs}_{0.25}\text{PbI}_3$. The CBM and VBM are dominated by the contributions from 6s orbitals of Pb and 5p orbitals of I. Color scale: red is defined as 0 and blue as $0.00015 \text{ e}\text{\AA}^{-3}$.

In contrast to the VBM, the CBM is dominated by Pb 6p nonbonding orbital contributions shown in Fig. 7b,d (see pDOS Fig. S5). The localized nature of the electronic

charge density indicates predominantly ionic character. Despite the nonbonding character, as shown in Fig 6b (upper panel), the CBM energy level is also influenced by A-cation mixing in these hybrid perovskites. The charge density contours of the CBM in FAPbI₃ and in the high Cs content system FA_{0.75}Cs_{0.25}PbI₃ (Fig. 7a, b) show that A-cation mixing enhances the contribution of 5p-I orbitals to the conduction band, inducing partial covalent character. The pDOS for the conduction band edge of FA_{1-x}Cs_xPbI₃ ($0 \leq x \leq 0.25$, Fig. S6) also demonstrate the increased participation of 5p-I orbitals in this band with A-cation mixing. Such a variation in conduction band position with structural distortion is in line with previous computational studies on inorganic and hybrid lead halide perovskites.^{64,76,77}

Due to the pseudo Jahn-Teller effect, the symmetry-lowering distortion in the inorganic framework of APbI₃ perovskites increases the covalency of the Pb-I bond.⁸⁰ The increased covalent nature in the largely ionic CBM shifts the band to higher energy as shown in Fig. 6b. Thus, the A-cation mixing affects the VBM and CBM in opposing ways, leading to an increase in the band gap. Recent X-ray and ultraviolet photoelectron spectroscopy experiments have also found a similar change in the energy levels in these mixed FA/Cs perovskites.³³

As noted in previous studies, single A-cation perovskites such as MAPbI₃ can exhibit a Rashba-type effect where the spin degeneracy of the conduction and valence bands are lifted, which can also lead to an indirect band gap.⁸¹⁻⁸⁵ We now consider the structural distortions from FA/Cs ion size mismatch on activating the Rashba-type spin-splitting^{86,87} of the CBM and VBM, resulting in substantial modifications of the band edges of FA_{1-x}Cs_xPbI₃.^{77,88} It is known that in the presence of heavy nuclei with high spin-orbit coupling constants, the Rashba-type effect spin-splits the band edges of materials which lack the local or extended inversion symmetry in their structure. To examine this effect, we have calculated band structures for FAPbI₃ and FA_{0.75}Cs_{0.25}PbI₃ as shown in Fig. 8.

Along both the $M \rightarrow \Gamma$ and $R \rightarrow \Gamma$ directions, the \mathbf{k} -dependent spin-splitting of the conduction band shifts the band extrema from the high symmetry Γ -point for the mixed

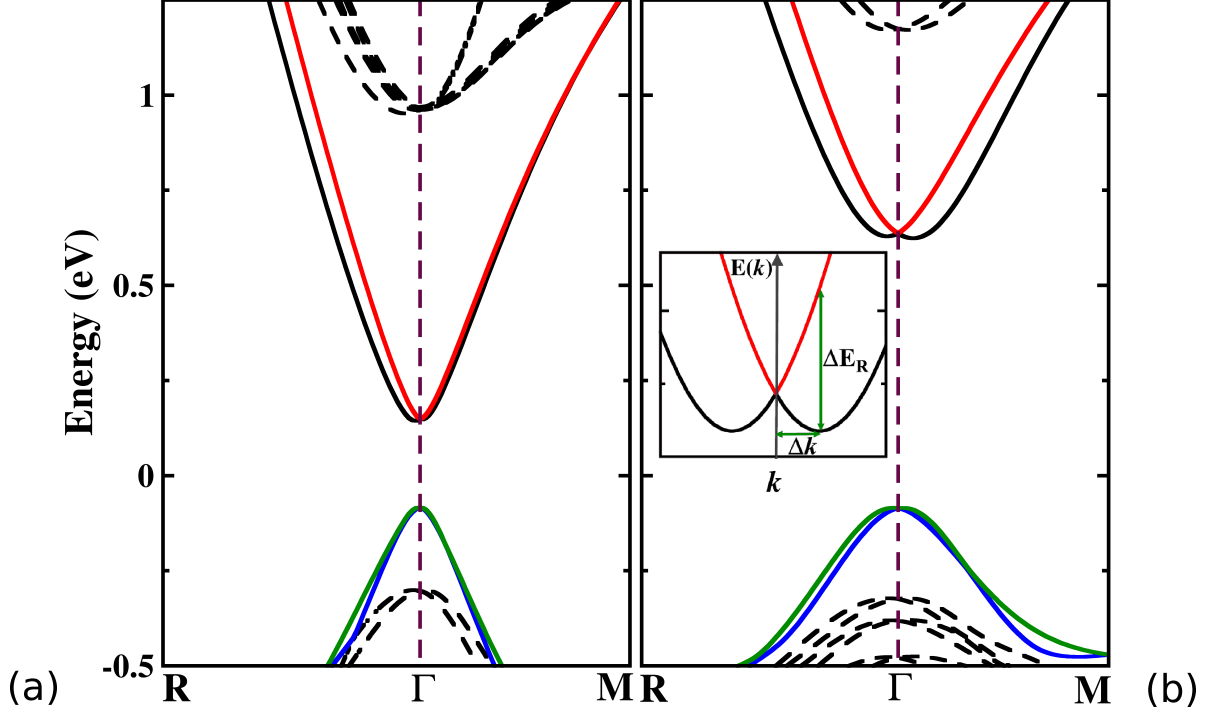


Figure 8: The Rashba-type effect in mixed A-cation perovskites. The PBEsol-SOC electronic band structures of (a) FAPbI_3 and (b) $\text{FA}_{0.75}\text{Cs}_{0.25}\text{PbI}_3$. The Rashba-Dresselhaus splitting of the CBM in the $\text{M} \rightarrow \Gamma$ and $\text{R} \rightarrow \Gamma$ directions for $\text{FA}_{0.75}\text{Cs}_{0.25}\text{PbI}_3$ is prominent. Inset of (b) shows zoomed version of splitted conduction bands. The spin-splitted valence bands are shown in green and blue solid lines. The conduction bands are represented by black and red colored solid lines. All other bands are represented by dashed black lines.

A-cation perovskite lattice. The momentum offset, $\Delta\mathbf{k}$ is the difference between the Γ -point and shifted band-extrema in k -space. For $\text{FA}_{0.75}\text{Cs}_{0.25}\text{PbI}_3$, $\Delta\mathbf{k}$ in the $\text{M} \rightarrow \Gamma$ and $\text{R} \rightarrow \Gamma$ high symmetry directions are 0.025 and 0.018 \AA^{-1} , respectively. $\Delta\mathbf{k}$ for such splitting in its valence band is much lower with a value of only 0.001 \AA^{-1} along both directions. The differing extents of $\Delta\mathbf{k}$ in the frontier bands creates an indirect band gap for $\text{FA}_{0.75}\text{Cs}_{0.25}\text{PbI}_3$ (see Table S1). Fundamentally, the Rashba-type splitting is directly related to the strength of the spin-orbit coupling of elements. Hence, the conduction band, which is dominated by contributions from heavy Pb atoms (Fig. 7a,b), splits more than the valence band, in which the lighter I atoms largely contribute (Fig. 7c,d). For FAPbI_3 , however, the extent of spin-splitting in the conduction band along $\text{M} \rightarrow \Gamma$ and $\text{R} \rightarrow \Gamma$ directions (Figure 8a,b) is significantly lower than in $\text{FA}_{0.75}\text{Cs}_{0.25}\text{PbI}_3$ (Figure 8c,d); in these two directions, $\Delta\mathbf{k}$

values for the conduction band in FAPbI₃ are only 0.002 and 0.003 Å⁻¹ respectively. Thus, considering static structures, the presence of greater symmetry-breaking distortion in mixed A-cation perovskites results in higher Rashba-type spin-splitting than in FAPbI₃.

The strength of the Rashba-type effect can be represented by the parameter $\alpha = E_R/2\Delta k$, where E_R is the amplitude of the band splitting in a particular direction (see inset of Fig. 8c). In FA_{0.75}Cs_{0.25}PbI₃, the estimated α values in the M → Γ and R → Γ directions are 0.96 and 0.88 eV Å, respectively, which are of the same order as reported by previous computational studies of related FA-iodide perovskites.⁸⁹

Interestingly, several experimental reports based on time-correlated single-photon counting measurements have demonstrated an increased carrier lifetime for the FA_{1-x}Cs_xPb(I_{0.6}Br_{0.4})₃ ($x \leq 0.25$).^{18,20} Better crystallinity and removal of non-perovskite phases by A-cation mixing have been argued as the primary causes for the improved photovoltaic properties.²⁰ Our results suggest that changes in the static and dynamic interactions between organic cation and inorganic Pb/I components in these mixed FA/Cs perovskites can also play an important role in the charge-carrier recombination. As shown in Fig. 8, structural distortions induce the Rashba-type spin-splitting of band edges resulting in an indirect band gap in FA_{0.75}Cs_{0.25}PbI₃. As a consequence of the indirect nature of the band gap in these distorted perovskites, photogenerated carriers occupy the band extrema with different k-points in reciprocal space. This, in turn, may reduce the possibility of radiative electron-hole recombination, which is otherwise active in direct band gap semiconductors. In the radiative limit an indirect band gap can affect the recombination rate for materials with low charge carrier mobilities and smaller absorption coefficients for indirect over direct optical transitions.⁹⁰ Due to other complex factors such as defect densities and transitions from defect states, assessing the exact influence of an indirect band gap on non-radiative recombination rates is not straightforward and requires further in-depth study.

We have shown that structural distortion from FA/Cs ion size mismatch makes these mixed A-cation structures less dynamic and induces static symmetry-breaking. Hence, we

suggest that under certain conditions static Rashba-type spin-splitting can be a significant factor for charge-carrier recombination processes in these mixed A-cation perovskites. It should be noted that our finding of a static band-splitting mechanism is different from the recently demonstrated dynamical Rashba effect in MAPbI₃ which appears from dynamical local symmetry breaking at finite temperatures.^{91,92} We recognize that other influences on recombination have been considered in the much-studied MAPbI₃ including carrier trapping, polaronic screening and an inverse absorption process.^{40,93} Nevertheless, Rashba-type effects on the optoelectronic properties warrant further experimental studies as discussed by Stranks and Plochocka.⁹⁴ Such effects have also rendered hybrid perovskites as promising materials for spintronic applications.^{88,94}

4. Conclusions

The changes in structural and optoelectronic properties of mixed A-site cation perovskite halides are not fully understood at the atomic-scale. We have investigated the mixed cation system FA_{1-x}Cs_xPbI₃ using a combination of static and dynamic *ab initio* simulations with the following key features emerging:

a) Incorporation of Cs⁺ cations into the parent FAPbI₃ compound induces significant structural distortion through ion size mismatch between the formamidinium ion (CH(NH₂)₂⁺, FA⁺) and the much smaller caesium ion (Cs⁺). This results in octahedral tilting and stronger N-H ··· I hydrogen bonding between the organic FA cation and iodide ions (within the inorganic cages), which help to stabilize the structure and promote greater thermal stability.

b) We find that the dynamic tilting of PbI₆ octahedra and rotational motion of FA-cations are significantly inhibited in the mixed cation structure, which leads to static symmetry-breaking of the lattice.

c) The band gap can be tuned by compositional cation substitution. The calculated band gap is found to widen with increasing Cs content in FA_{1-x}Cs_xPbI₃ as observed experimen-

tally. The alignment of frontier energy levels are also altered by the structural distortions. The symmetry-breaking distortions of the Pb/I lattice give rise to the Rashba-type effect, which spin-splits the frontier electronic bands making the band gap indirect. Our results suggest that the direct to indirect band gap transition may be a factor in the reduced rate of charge-carrier recombination in mixed A-cation perovskites.

These findings warrant further investigation and, indeed, one of the aims of our work is to stimulate new experimental studies in this area.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Detail methods, phase stability, octahedral tilting, hydrogen bonding analysis and reorientation relaxation time.

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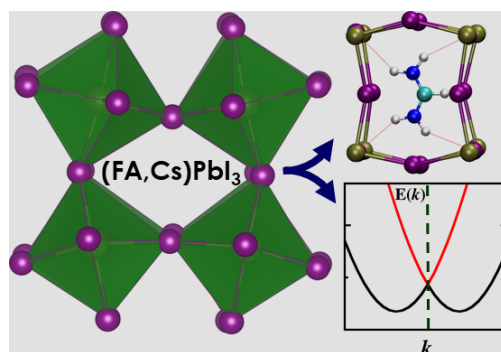
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Supporting Information

Mixed A-Cation Perovskites for Solar Cells: Atomic-Scale Insights Into Structural Distortion, Hydrogen Bonding and Electronic Properties

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S1. Methods

S1.1 Crystal structure and Cation-disordering in FAPbI₃

To model the perovskite phase of FAPbI₃, we have considered the high symmetry cubic structure as reported by Weller *et al.*¹ We kept the cell parameters fixed to their experimental values and fully relaxed the geometry. Relaxing the lattice parameters during geometry optimization also results in very similar ground state structures. To model the disordered FA⁺ cations in static DFT-based simulations, we performed cell and geometry optimizations of 40 different 4×4×4 supercells, and in each case the orientation of the FA⁺ cations were ran-

domly generated. The difference in ground-state energies among these systems is very small (< 25 meV/f.u.) as shown in Fig. S1. Thus, FA^+ cation orientation does not significantly affect the ground-state energy of FAPbI_3 .

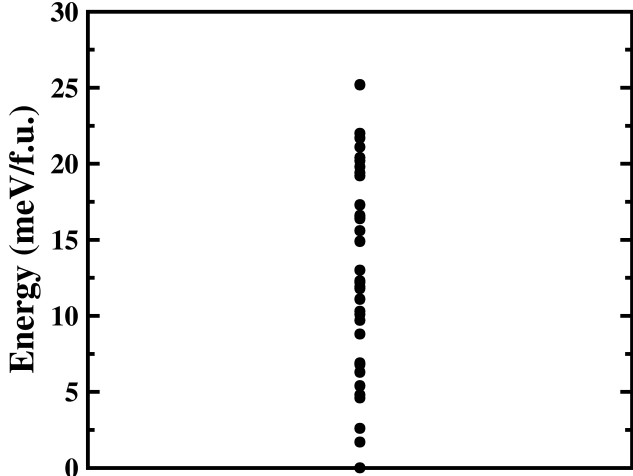


Figure S 1: Ground state energy of FAPbI_3 with different randomly generated FA^+ cation orientations. The difference in energies is < 25 meV/f.u. The energy values are scaled to the lowest energy structure. The structural optimizations were performed using the CP2K package.

To explore the effect of the relative arrangement of the cations, we consider various configurations with different ordering of FA^+ and Cs^+ cations in $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$. The configurations with dispersed Cs^+ cations always give rise to the most stable geometries (Fig S2). We have thus considered configurations with well dispersed Cs^+ cations in all the $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ ($0 < x < 0.25$) compositions.

S1.2 Crystal structure of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$

The geometry and cell parameters for $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ ($0 \leq x \leq 0.025$) structures are fully optimized during the relaxation process. The calculated cell parameters and systematic reduction in cell volume, are in good agreement with recent experimental reports.^{2,3}

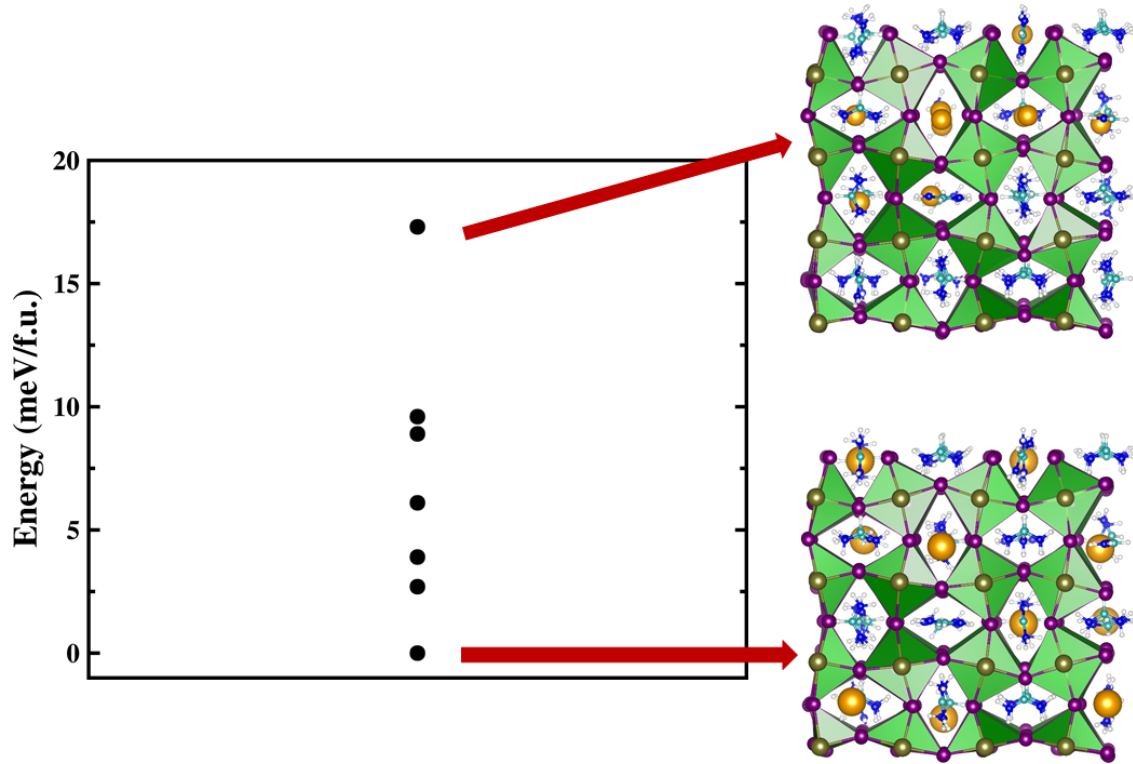


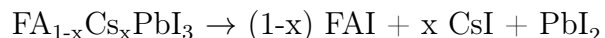
Figure S 2: Ground state energy of $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ with a random distribution of FA^+ and Cs^+ cations. The simulation cells with lowest and highest ground-state energy are shown. The structural optimizations were performed using the CP2K package.

1.3 Band-alignment in mixed A-cation perovskites

As a direct comparison of the Kohn-Sham orbital energies is conceptually difficult due to the lack of a proper reference state, several alternative approaches have emerged. One of these consider localized deep states (impurity or atomic) which are not influenced by the bonding pattern, as the reference state. Here, we have considered the deep-level nd -orbitals of Pb as the reference state. A similar approach has been successfully applied to other lead halide perovskite systems.^{4,5}

1.4 Helmholtz Free Energy of Mixing and Decomposition Enthalpy

Previous experiments find that these perovskites degrade into the halide components i.e. PbI_2 , FAI, and CsI.⁶ Thus, the decomposition reaction can be considered as,



The decomposition enthalpy change can be formulated as,

$$\Delta H = (E_{\text{PbI}_2} + (1 - x)E_{\text{FAI}} + xE_{\text{CsI}}) - E_{\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3} \quad (1)$$

where, $E_{\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3}$, E_{PbI_2} , E_{FAI} and E_{CsI} are the total ground state energy/formula unit of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$, and the decomposed products, PbI_2 , FAI and CsI in their corresponding most stable phase, respectively. As the equation suggests, the positive value of enthalpy indicates that the reaction is endothermic and thus the perovskite phase is thermodynamically stable against the decomposition process. Note that as we calculate the total energies of these chemical species from zero temperature DFT-based method, we exclude zero-point vibrational energy which has a negligible contribution.⁷ The calculated values of decomposition enthalpy show that the reaction becomes exothermic to endothermic upon the incorporation of Cs in FAPbI_3 .

We further investigate the thermodynamic stability of $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ against spontaneous phase-separation to the most stable phase of the parent perovskites which are hexagonal- FAPbI_3 and orthorhombic CsPbI_3 . Considering basic thermodynamics, as the volume change with A-cation mixing is negligible in these perovskites, the Helmholtz free energy (F) can replace the Gibb's free energy to determine true thermodynamic stability of the solid-solution.^{5,8} The Helmholtz free energy can be formulated as follows,

$$\Delta F = \Delta U - T\Delta S \quad (2)$$

where ΔU and ΔS are the internal energy and entropy of mixing, respectively and T is the temperature. Here, we apply the generalised quasi-chemical approximation to calculate these thermodynamic quantities.⁸ The internal energy of mixing has been calculated from the following equation,

$$\Delta U = F_{\text{A}_{1-x}\text{Cs}_x\text{PbI}_3} - (1 - x)F_{\text{FAPbI}_3} - xF_{\text{CsPbI}_3} \quad (3)$$

Considering a homogeneous distribution of A-cations, we calculate the entropy of mixing as,

$$\Delta S = -k_B[x\ln x + (1 - x)\ln(1 - x)] \tag{4}$$

where k_B is the Boltzmann constant.

The Helmholtz free energy at 300 K indicates that the solid solution of FA/Cs cations in $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ is thermodynamically more favourable than the phase-separated compounds.

S2. Phase Stability of FAPbI_3

FAPbI_3 crystallizes in a hexagonal yellow phase (termed δ -phase) with space group $\text{P6}_3/\text{mc}$ at room temperature.⁶ The cubic black phase (α -phase) which is the desired phase for solar-cell applications, appears only at high temperature. To validate our DFT-based computational approach, we examined the optimized structures and relative phase-stability of these two phases at 0 K. Considering the ground-state energies, the δ -phase of FAPbI_3 appears to be more stable than the α -phase by 0.12 eV/f.u. We further calculate the decomposition enthalpy to investigate the stability of these different phases of FAPbI_3 against the experimentally observed decomposition to PbI_2 and FAI . Although the δ phase is energetically stable, the α phase is much more susceptible towards such decomposition. The phase-stability order as well as stability against decomposition are in good agreement with the previous experimental observations and thus validate our approach.⁶

S3. PbI_6 Octahedra in $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$

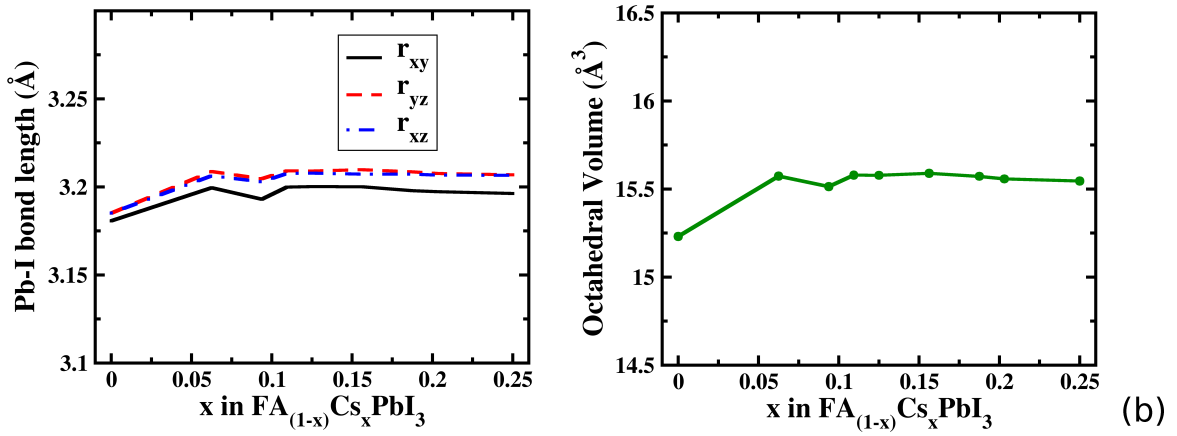


Figure S 3: Internal structure of PbI_6 octahedra: (a) average Pb-I bond-lengths in different Cartesian planes and (b) average volume of PbI_6 octahedra for FAPbI_3 and $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ ($0 \leq x \leq 0.025$). Upon A-cation mixing average Pb-I bond lengths and volume remain largely unaffected, indicating the unaltered internal geometry of the PbI_6 octahedra in these perovskites.

S4. Octahedral tilting in $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$

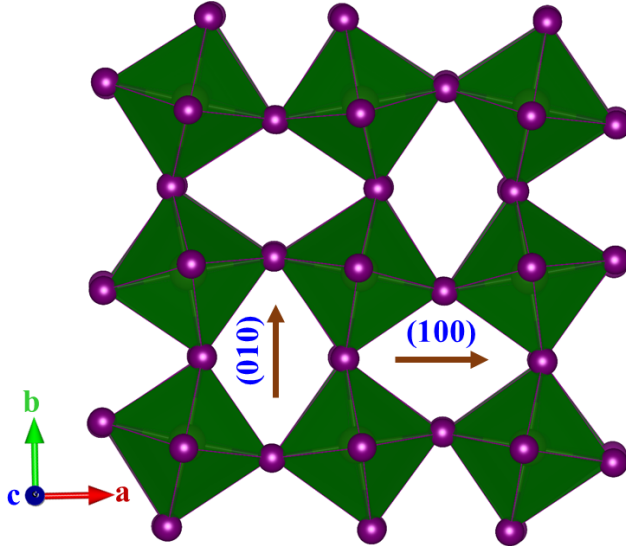


Figure S 4: Time-averaged equilibrated structure of $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ from *ab initio* molecular dynamics simulations. The cuboctahedral cages elongate in the [100] or [010] lattice directions, shown by the brown arrows. The FA^+ cations also orient themselves in these directions. Octahedra rotate mainly in the *ab*-plane, keeping the Pb-I-Pb bond angles along the [001]-axis of the crystal at $\approx 180^\circ$. Key: purple - iodine; green - PbI_6 octahedra.

S5. Hydrogen bonding in hexagonal $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$

The hexagonal phase of FAPbI_3 contains one-dimensional PbI chains with face sharing PbI_6 octahedra, and with the FA cations remaining intercalated between layers (see Fig. S5 a). The $\text{H}_\text{N}\cdots\text{I}$ distances are now $\sim 2.88 \text{ \AA}$ to 3.31 \AA which are longer than that in the perovskite phase of FAPbI_3 . Unlike in perovskite phase, A-cation mixing does not distort the hexagonal lattice (see Fig. S5 b). The cation - lattice interaction is retained almost unchanged with respect to the parent hexagonal FAPbI_3 . This in turn indicates that the enhanced phase stability due to stronger hydrogen bonding interactions only occurs in the perovskite phase of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$. As observed experimentally,^{5,9,10} this could be a key factor in stabilizing the perovskite phase of these mixed cation systems against the hexagonal phase.

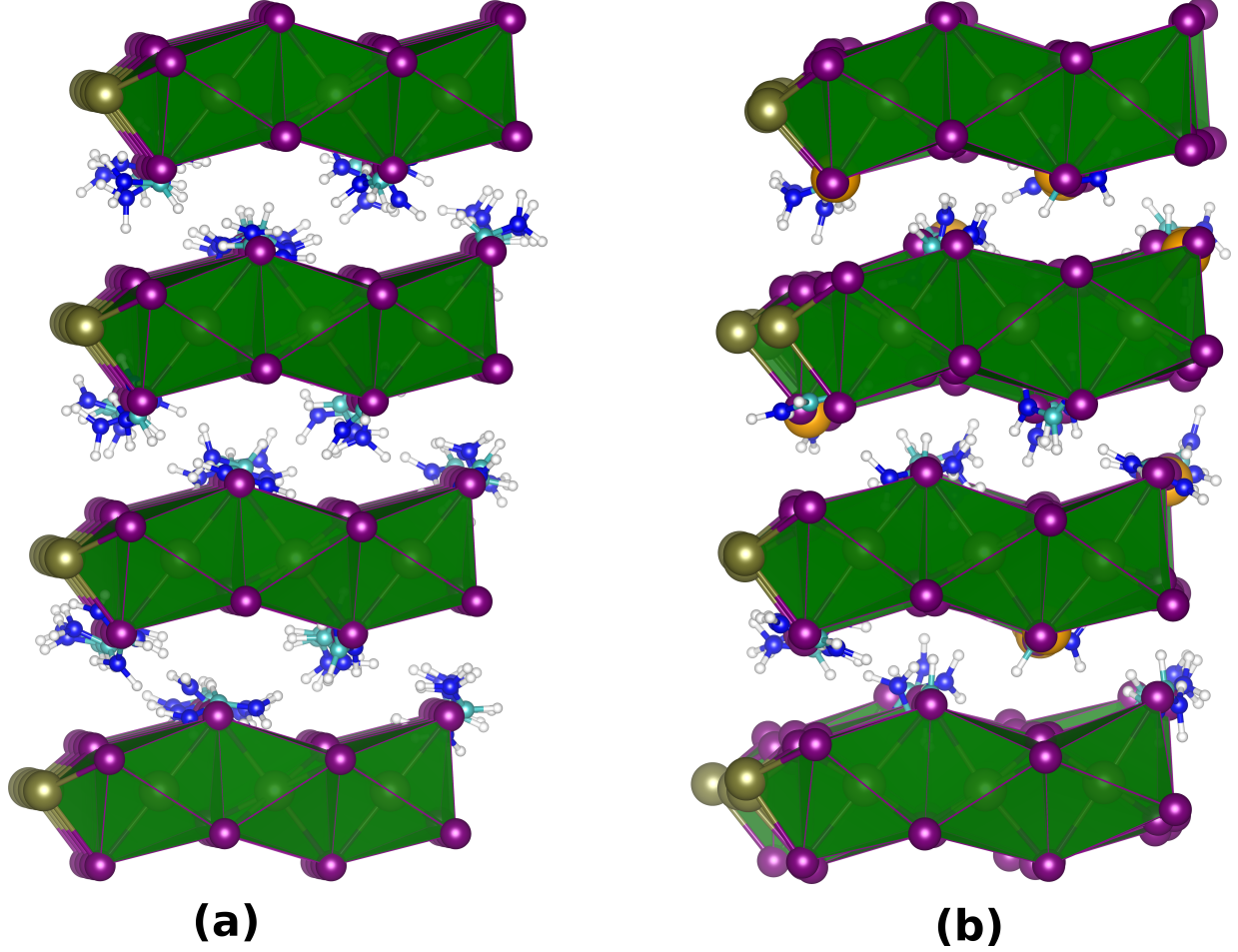


Figure S 5: Optimized geometries of hexagonal phase of (a) FAPbI_3 and (b) $\text{FA}_{0.75}\text{Cs}_{0.25}\text{PbI}_3$.

S6. Calculation of the reorientational relaxation time

In order to investigate cation dynamics, we analyze the vector reorientation function of FA^+ in the parent and in mixed A-cation systems. This is an autocorrelation function of the molecular vector ($\hat{\mathbf{n}}$), formulated as the normalized sum over the scalar product between the vector at time t' and the same vector at $t' + t$, considering all initial times t' .¹¹ The autocorrelation function can be represented as,

$$c(t) = N. \left\langle \sum_{t'=0}^{T-t} \hat{\mathbf{n}}_i(t') \cdot \hat{\mathbf{n}}_i(t' + t) \right\rangle_i \quad (5)$$

where \mathbf{n} is the molecular vector, N is the normalization factor and T is the total simulation time.

Due to the non-exponential decay of the vector autocorrelation functions, we fit these functions with stretched exponential functions,

$$f(t) = \exp(-t'/t)^\beta \quad (6)$$

We find the best fit of the autocorrelation function in cubic FAPbI_3 and $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ for β values of 0.64 and 0.48, respectively.

S7. Band Gap of FAPbI_3 and $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ with PBEsol-SOC

Table S 1: Band Gap with PBEsol-SOC

Perovskite	Direct Band Gap (meV)	Indirect Band Gap (meV)
FAPbI_3	227	226
$\text{FA}_{0.75}\text{Cs}_{0.25}\text{PbI}_3$	722	708

S8. Density of States for FAPbI₃

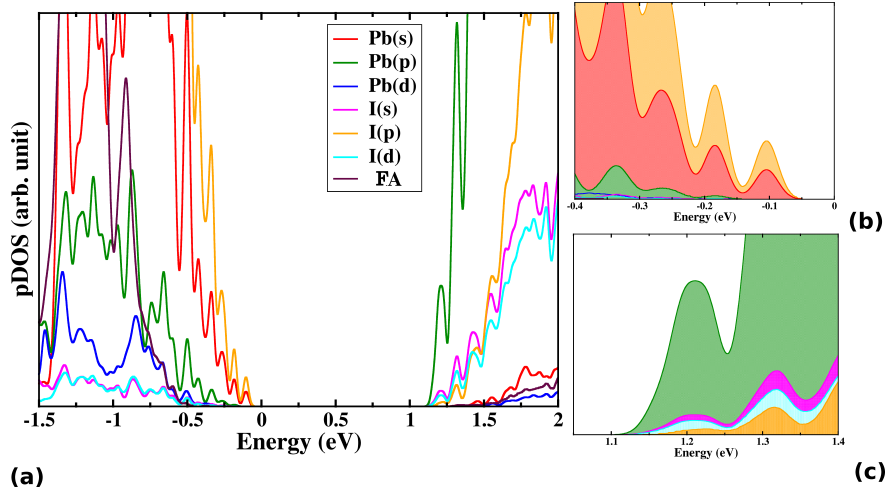


Figure S 6: (a) Partial density of states (pDOS) for FAPbI₃. The zoomed view of band edges (b) valence band and (c) conduction band are shown. The pDOS of these states indicate the covalent and ionic nature of the valence and conduction bands, respectively.

S9. Orbital contributions of FA_{1-x}Cs_xPbI₃ to the CBM

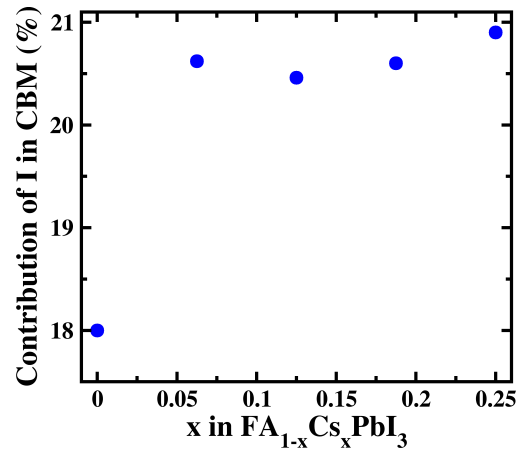


Figure S 7: The summed-up contribution of iodine orbitals to the conduction band minima, CBM, with varying concentration of Cs⁺ in FA_{1-x}Cs_xPbI₃.

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