

Light-Induced Frenkel Defect Pair Formation Can Lead to Phase-Segregation of Otherwise Miscible Halide Perovskite Alloys

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Alloys of ABX_3 halide perovskites (HP) exhibit unique phase behavior compared to traditional III-V and II-VI semiconductor alloys used in solar cells. While the latter typically have good mutual miscibility when their mixed components are size matched, and phase-segregate when size mismatched, HP alloys show good miscibility in the dark but can phase-segregate under light. Quantum mechanical calculations described herein reveal light-induced defect formation and migration hold the key. Specifically, the interaction between a halogen vacancy V_X with halogen interstitial X_i forming together a Frenkel-pair defect emerges as the enabler for phase-segregation in HP alloys. At a threshold bromine composition in the Br-I alloys, the photogenerated holes in the valence band localize, creating thereby a doubly-charged iodine Frenkel-pair $(V_i + I_i)^{2+}$. Faster migration of iodine over bromine interstitial into the vacant iodine V_i site leads to the formation of iodine-rich and iodine-depleted regions, establishing phase-segregation. Removal of the mobile defects—the agent of segregation—by dark thermal annealing, supplies the opposing force, leading to reversal of phase-segregation. This atomistic understanding can enable some control of the phase-segregation by selecting substituting elements on the B site—such as replacing some Pb by Sn—that are unable to form stable Frenkel defects.

yet as being optimal for such applications. Consequently, *alloying* two or more individual ABX_3 halide perovskite components has been generally imposed by the need to tune the band gap values into a desired spectral range for either a single junction or tandem solar cells.^[5,6] It is well known that alloying of tetrahedrally bonded covalent semiconductors such as different III-V's or different II-VI's generally leads to mutual miscibility if the atomic sizes tend to be sufficiently size-matched, and to phase-separate below a given miscibility temperature if their atomic sizes are sufficiently mismatched.^[7–9] However, alloys of HP components behave differently. For example, while alloying two HPs with different halogen ions X and X' can lead to their complete miscibility in the dark, Hoke et al.^[10] demonstrated that $MAPb(Br_xI_{1-x})_3$ alloys (where MA stands for methylammonium) phase-segregate into their end-point parent compounds $MAPbI_3$ and $MAPbBr_3$ under brief light exposure. This phase segregation

process is reversible under annealing,^[10] and has been observed since then in many other iodine-bromide perovskite alloys for different A-cations, whether organic (such as $MAPb(Br_xI_{1-x})_3$, $FAPb(Br_xI_{1-x})_3$) or inorganic $[CsPb(Br_xI_{1-x})_3]$.^[10–12] While it originally appeared that this light induced phase separation of otherwise miscible components is specific to HP with organic A molecular cations, recent experimental studies indicated that even the inorganic Cs-based HPs, e.g., $CsPbBrI_2$ manifest such an effect under a long light exposure.^[12] As can be readily imagined, such light-induced compositional phase-separation is an unwanted response for photovoltaic devices aimed at operating under (sun) light. Partial mitigation of this effect has been empirically demonstrated by limiting the percentage of Br in the alloy, or by simultaneous alloying the A-site by Cs and organic molecules,^[12] or by co-alloying the B site by Sn and Pb.^[13] Yet, these solutions leave the underlying question unanswered: what is the physical source of miscibility in the dark and segregation under the light in HP mixed anion alloys, a phenomenon which stands out relative to alloys of more conventional tetrahedral semiconductors?

Attempts to understand the light induced phase separation of otherwise miscible HP components included a few

1. Introduction

Halide perovskites (HP) $A^{(I)}B^{(II)}X_3^{(VII)}$ where A is a monovalent cation, B is a divalent group IVA metalloid and X is a halogen anion rose to public awareness due to their unprecedented efficacy in photovoltaic (PV) solar cells.^[1–4] Even though different choices of the {A, B, X} species occupying the respective lattice sites of the perovskite lattice can lead to a significant range in the semi-conducting band gap energy, no single perovskite has emerged

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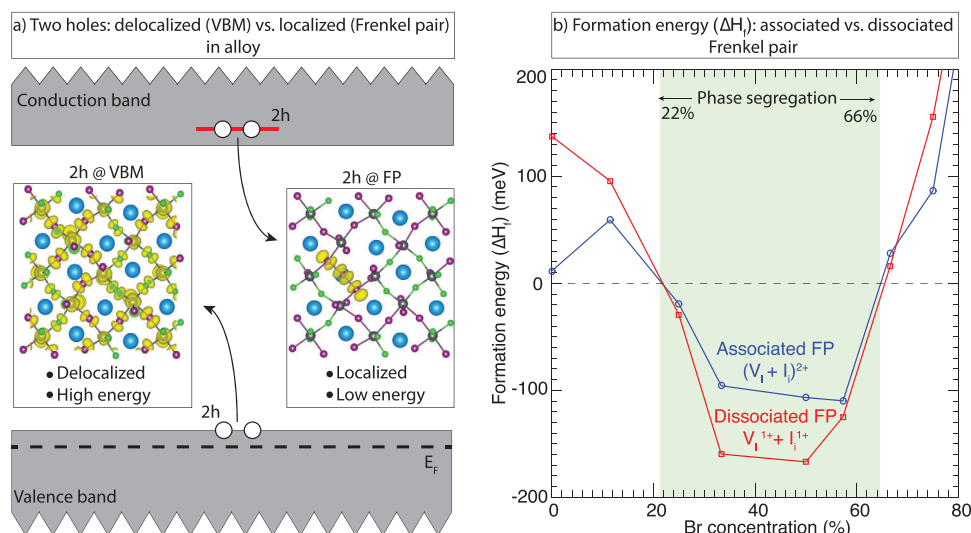


Figure 1. (a) Electronic energy level scheme in valence and conduction bands and orbital density (yellow isosurfaces) depiction of delocalized holes at the valence band maximum (left hand side), and hole localized with the Frenkel pair orbitals located in resonance at the conduction band (right hand side). The purple atoms represent I, the gray Pb, green Br, and Blue Cs. (b) Formation energy of “associated” Frenkel pair (blue) and “dissociated” components (red) with different alloy background Br compositions x . The values are calculated according to the equations in Technical Details for the iodine interstitial plus iodine vacancy, forming the iodine Frenkel pair (FP). The formation energy of an associated FP (Blue line) shows that it is favorable (has negative energy) in the intermediate Br compositions (green shaded background) but is unfavorable in the low or high Br compositions. The red line shows the energy of dissociated FP, that is when its two components $[V_I^{1+} + I_I^{1+}]$ are separated.

views. *Thermodynamic models:* Walsh et al.^[14] pointed out that the temperature-composition phase diagram of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ should exhibit spinodal decomposition below $T \sim 300\text{K}$ and for $0.3 < x < 0.6$. However, this does not explain the segregation under light and remixing under dark. Kuno et al.^[15,16] measured the activation energy for phase segregation and remixing in the dark of $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$, indicating that light makes the phase segregation thermodynamically favorable. *Role of intrinsic defects:* Photoinduced ‘large polarons’ in highly ionic compounds can induce strain in the lattice and increase the Gibbs free energy, leading to ions migration and promoting phase segregation.^[17,18] Another approach includes addressing the halogen vacancies and halogen interstitial path for atoms diffusion.^[19–22] Light can activate halogen diffusion, where the diffusion ratio is different for I and Br; this can result in selective sample domains that are either rich or depleted of I, leading to alloy segregation.^[19–22] Recent experimental studies by Kamat et al. demonstrate that self-degradation is associated with diffusion.^[11,19,23] When $\text{MAPbI}_{1.5}\text{Br}_{1.5}$ is in contact with an electrolyte and under charge injection, it is possible to observe an increase in the concentration of I_{3-} ions in the electrolyte supporting the fact that there is iodine expulsion from the alloy.^[19] Moreover, they demonstrate that the main cause of phase segregation is the holes excess and not the electrons. The holes can be introduced in the HPs by light or electrochemically while the electrons are removed by a contact with a Fermi level lower than the alloy conduction band. Kamat et al. have explained the segregation through a mechanism that starts from holes capturing in the iodine interstitial sites.^[19] However, first-principles calculations demonstrate that the halogens interstitials tend to be in the positive charge state when the Fermi level lies close to the valence band,^[24] and therefore could not be the source of holes (induced by light) capture during the phase segregation.

In the present paper, DFT calculations were done in the alloy supercells to unravel an explanation for the phase segregation in Br-I alloys of halide perovskites; rather than assume pre-existing holes bearing defects before illumination, here photoexcitation creates the relevant complex defect. The hole rich conditions observed in the recent experimental results were considered in our analysis.^[23]

Frenkel defects are created under light illumination: initially, the Fermi energy is shifted in an Iodine-Bromine alloy $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$, to create valence band holes. We then inspect the DFT orbital densities after atomic relaxation to see if these holes are conventionally delocalized (i.e., hydrogenic shallow acceptor), or prefer to lower the energy by localizing the holes in specific locations. An example is the iodine Frenkel pair (FP) made of iodine interstitial and iodine vacancy close to each other, indicated in the schematic **Figure 1a**. The Frenkel pair, and other complex defects were recently discussed in the energy level diagram to describe the mixed electronic and ionic conductivity in halide perovskites.^[25]

Figure 1b shows the formation energy of an associated FP (associated means that halogen vacancy is closer to the halogen interstitial), in blue line, is favorable (negative energy) for intermediate Br compositions, i.e., two holes at valence band maximum (VBM) localize and create an iodine Frenkel pair. For the same range of Br compositions, the *dissociated* iodine FP (dissociated means that the halogen vacancy is treated without interaction with halogen interstitial) formation energy red line in (Figure 1b) is lower in energy (more stable) than the associated FP, indicating that, in case the iodine Frenkel pair forms, it tends to separate into iodine interstitial and iodine vacancy. Due to the larger mobility of I ions relative to Br,^[19–22] the I ions will migrate and form I-rich and Br-rich regions. As Figure 1b shows, when the Br

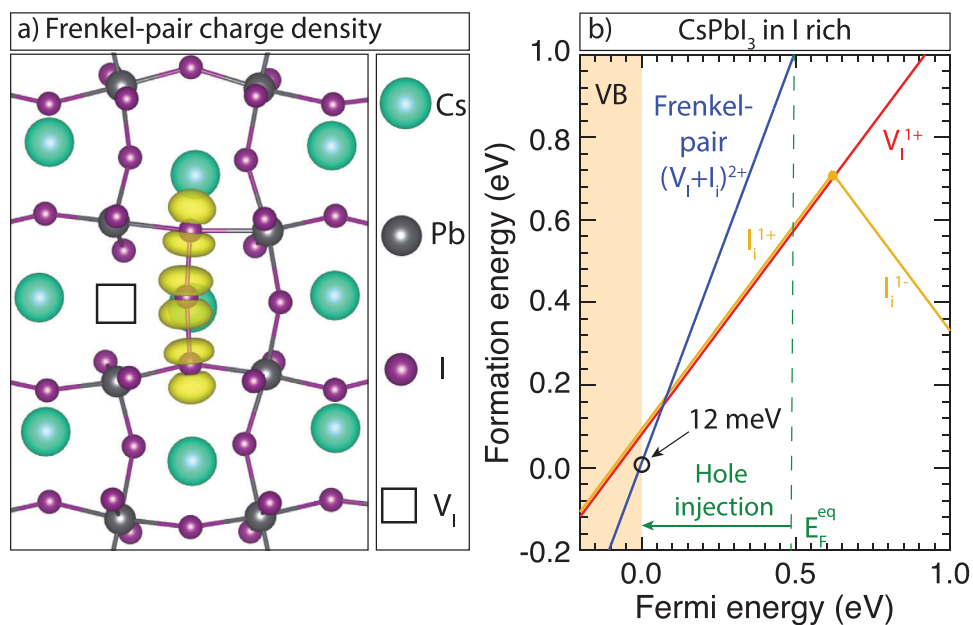


Figure 2. (a) Charge density isosurface for the state that corresponds to the Frenkel pair (V_I+I_I) in the 2+ charge state in CsPbI_3 . (b) Formation energy as a function of Fermi energy for Frenkel pair (V_I+I_I), vacancy of I (V_I), and iodine interstitial (I_I). The green line indicates the position of the equilibrium Fermi level for I rich condition. The black arrow indicates the formation energy of Frenkel pair when the Fermi level is closer to the valence band.

concentration is outside the shaded green area, the formation energy, the formation energy of the FP becomes positive, meaning the hole at the VB does not tend to spontaneously localize in forming a FP. At this point, the segregation process stops.

In the absence of illumination, the Frenkel pair is unlikely to form because of its high formation energy when the Fermi level is away from the valence band, so phase segregation cannot occur. The remixing alloy process occurs under dark and with high temperature annealing, which promotes the halogen migrations, and the previous photoinduced halogen interstitial cancels the previous photoinduced halogen vacancy, returning to the similar alloy mixed configuration.

This process of light-induced formation of dissociated iodine Frenkel pairs in the intermediate alloy composition range and the I migration through the lattice leads to I vs Br phase separation. In the low and high Br alloy composition or in the dark the Iodine FP does not form so the phase segregation does not occur. We further find in the calculation that FP does not form in halide perovskites with Sn at the B site, even in the hole rich condition. Consequently, Sn-rich conditions will avoid segregation, in agreement with the experimental results.

1.1. Computational Methodology

The first-principles calculations are based on the density functional theory as implemented in the Vienna ab-initio simulation package (VASP).^[26,27] Structural relaxation is performed by using a semi-local generalized gradient approximation (PBEsol).^[28] The electronic structure and all the defects' properties were carried out with the hybrid Heyd-Scuseria-Ernzerhof (HSE)^[29,30] with the addition of spin-orbital coupling. For the HSE functional, we used 43% of exact exchange, which is necessary to cor-

rect the band gap of all systems calculated here. More technical details of computational parameters are described in the Technical Details section.

The ground state structure (low temperature) for CsPbI_3 and CsPbBr_3 is the orthorhombic Pbnm. However, in our analysis, we considered only the cubic perovskite structure because this crystal structure is important for solar cell applications closer to room temperature. To simulate the cubic structure of halide perovskites we need to use polymorphous configurations.^[31] In a supercell that corresponds to $2\sqrt{2}\times 2\sqrt{2}\times 4$ repetitions of Pm-3m cubic perovskites, containing 32 ABX_3 formula units (160 atoms), we apply a nudge operator in a random direction in all the atoms and let then relax through DFT calculations. The relaxed structure is composed of octahedral rotation, however, in space average, the cubic Pm-3m is maintained. All defects and electronic properties were computed in this polymorphous structure.

2. Results

The Frenkel pair is composed of the combination of one halogen interstitial with a first neighbor halogen vacancy, both related to the same chemical specie. The wavefunction squared of the iodine Frenkel pair defect is shown in **Figure 2a**. Our explanation of the main effects of phase segregation is based on the formation of this Frenkel defect, and consists of three different processes:

Delocalized holes or holes localized inside a FP: In the first stage it is described the competition between (i) photogenerated holes delocalized in the valence band and (ii) the localization of holes in the form of a Frenkel pair defect. Here, case (i) is obtained by shifting the Fermi level without atomic relaxation, whereas (ii) might occur after atomic relaxation. This stage reveals that in certain alloy compositions the delocalized holes will transform into

localized Frenkel pair as shown in Figure 1a. The significance of being localized on specific atoms is that it distinguishes migration that carries iodine to certain locations, but not Br. At low and high Br concentrations ($\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ with $x < 0.22$ and $x > 0.66$) the localized FP no longer exists and is replaced by delocalized holes; these have no atomic signature and thus are not agents of atomically-resolved phase separation.

Dependence of FP stability on the atoms: Br or I. In the second stage, we discuss the relative stability of Frenkel pair defects, where we show the condition to form the FP defect with respect to the local chemical environment and its charge states. We, therefore, tried different sites where the defects were created into the supercell, and investigate the most stable ones to form the Frenkel-pair.

Associated Frenkel pair or dissociated Frenkel pair. The Frenkel pair with associated components can dissociate into halogen vacancies and halogen interstitial which will culminate in the phase segregation and the formation of I and Br-rich regions.

All these stages will be discussed firstly for the parent compounds, i.e., CsPbI_3 and CsPbBr_3 (section 3.1); and afterward for the alloy $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ (section 3.2) in different x concentrations.

2.1. Frenkel Pair Formation in Non-Alloyed, Individual Halide Perovskite Compounds: CsPbI_3 and CsPbBr_3

Delocalized holes at the valence band or localized trapped holes in Frenkel pair defect: In this stage, it is examined the possibility of holes becoming localized in a FP (we use the formation energy expression given by Eq. (1) in the Technical Details. Note that the Frenkel pair formation energy is a quantity that is independent of the halogen chemical potential. Figure 2b shows the formation energy for the Frenkel pair defect of CsPbI_3 vs. the Fermi energy. Only the 2+ charge state is obtained. For E_F close to the VBM (hole-rich condition), the formation energy of the Frenkel pair is very low (equal to only 12 meV), which means that, at room temperature, the thermal energy is enough to generate the Frenkel pair defect. In contrast, if E_F lies in the middle of the band gap, as in the equilibrium Fermi level for I-rich condition (vertical dashed line in Figure 2b), the formation energy of Frenkel pair will be larger than 1.0 eV. Because of that, we do not expect the formation of Frenkel pair in CsPbI_3 far from the hole-rich condition.

The Frenkel pair can be viewed as a form of localization of holes around specific atoms/sites as shown in the charge isosurface in Figure 2a. The excess of holes, generated by light or introduced electrochemically, localizes and promotes the formation of Frenkel pair. The combination of hole localization and atomic displacement can also be described as a polaron, and in this condition, a small hole polaron. Different from other materials, such as oxides,^[32–35] the orbital energy of the polaron does not lie in the middle of the gap, but instead, is in resonance in the conduction band, as shown in the density of states in Figure 3a.

Calculations for the formation energy of the bromine Frenkel pair in CsPbBr_3 , namely $(\text{V}_{\text{Br}} + \text{Br}_i)^{2+}$, also were done. For E_F at the VBM, it was found a value of 0.79 eV (not shown in Figure 2). This is 65 times larger than the formation energy of iodine Frenkel pair in CsPbI_3 . One possible reason for this difference is the abso-

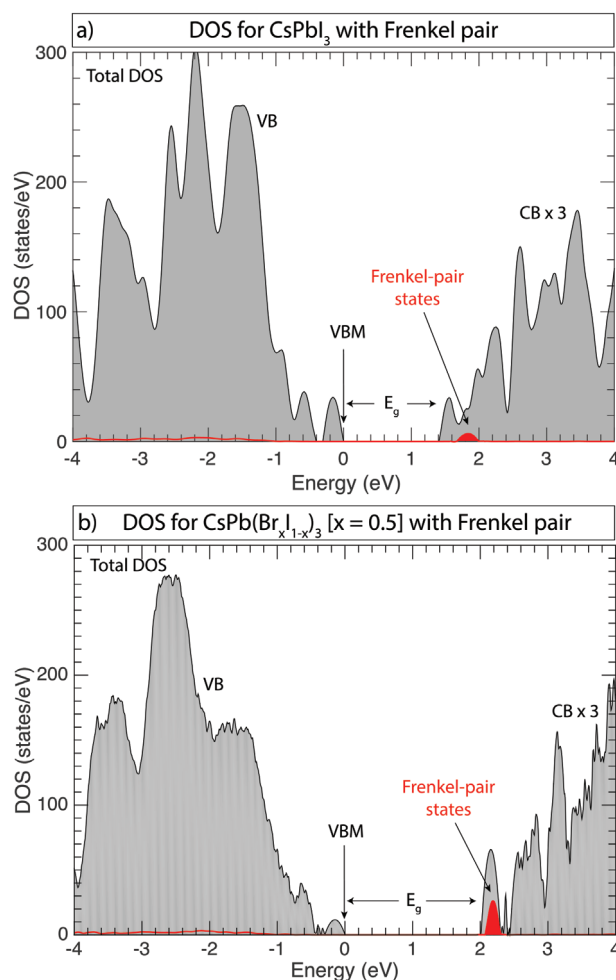


Figure 3. Density of states for a) CsPbI_3 and for b) $\text{CsPb}(\text{Br}_x\text{I}_{1-x})_3$ with $x = 0.5$. The red region indicates the Frenkel pair orbital states, which are in resonance at the conduction band. The valence band maximum for each case is set as 0 energy.

lute energy of the VBM of CsPbBr_3 which is deeper than the VBM of CsPbI_3 .^[36] As the VBM is deeper, the energy required to create holes will be larger, destabilizing the Frenkel pair. Another reason can be the higher complexation affinity of Pb^{2+} and Br^- when compared to the Pb^{2+} and I^- .^[37] Considering these points, we do not expect the formation of bromine Frenkel pairs in CsPbBr_3 even when the Fermi level is shifted down to the vicinity of VBM by hole injection.

Iodine Frenkel Pair vs Br Frenkel pair in single perovskite compounds: In this stage, it was checked the possibility of different sites for the Frenkel pair, and different charge states. For the compounds CsPbI_3 and CsPbBr_3 there is a unique combination of halogen vacancy and halogen interstitial to form the Frenkel pair, which results in $\text{V}_\text{I} + \text{I}_i$ and $\text{V}_\text{Br} + \text{Br}_i$, respectively. For both Frenkel pairs, we tested the following charge states: neutral, 1+, and 2+. Only in the 2+ charge state the Frenkel pair defects configuration is maintained. In other words, the DFT relaxation process in neutral and 1+ charge state moves the halogen interstitial towards the halogen vacancy, filling it and recovering the stoichiometric polymorphous atomic configuration. Therefore, the Frenkel

pair in the halide perovskites can exist only in 2+ charge state, i.e., hole-rich condition. From an experimental point of view, the hole-rich condition is obtained by light or electrochemical hole injection.^[19,23]

Associated or dissociated components of a Frenkel Pair. In Figure 2b we also report the formation energy for V_1 and I_1 treating them as dissociated components for CsPbI_3 . For E_F at the VBM and for the I-rich condition, both defects have almost the same formation energy of 0.10 eV. The formation energies of V_1 and I_1 have a dependence on the halogen chemical potential; while for I-rich there is a decrease in the formation energy of I_1 , the I-poor configuration decreases the formation energy of V_1 . However, the sum of both formation energies is independent of the halogen chemical potential, and this quantity can be used to determine the defects binding energy according to Eq. (2) of the Technical Details. The defects binding energy describes the energy necessary for two (or more) defects to stick together and form a complex defect, in our case, the associated Frenkel pair. For CsPbI_3 , the binding energy is equal to -0.13 eV, which indicates that there is an energy gain when I_1 and V_1 stick together to form the Frenkel pair when compared to the dissociated defects. For CsPbBr_3 , as mentioned before, the Frenkel pair has larger formation energy, and the binding energy is close to 0 eV. If the Frenkel pair could be formed, the room temperature is enough to dissociate the Frenkel pair into the defect composition.

Based on all three stages above, we can conclude for the non-alloyed HP:

- i. the Frenkel pair can exist only in an environment rich in holes, since it is stable only in the 2+ charge state, and therefore only in HP under light or hole injection.
- ii. The holes at the VBM in CsPbI_3 can localize to form the Frenkel pair defect.
- iii. The associated Frenkel pair in CsPbI_3 is more stable than the dissociated defects – V_1 and I_1 .
- iv. There is a large formation energy of Frenkel pairs based on Br, and we do not expect the existence of this complex defect in CsPbBr_3 .

2.2. Frenkel Pair Formation in Halide Perovskite Alloys: $\text{CsPb}(I_{1-x}\text{Br}_x)_3$

Delocalized holes at the valence band vs. localized at Frenkel pair in alloys: The calculation of Frenkel pair formation energy with E_F at the VBM and as a function of the alloy composition x is shown in Figure 1b. In the region with intermediate bromine composition ($0.22 < x < 0.66$, shown in the green area), the formation energy of Frenkel pair is negative, i.e., spontaneous formation. Therefore, the holes at the VBM localize and form the Frenkel pair $(V_1+I_1)^{2+}$ spontaneously as shown in the schematic Figure 1a. The orbital state of Frenkel pair lies in resonance in the conduction band, a similar condition of CsPbI_3 , and can be observed in the density of states calculation, Figure 3b.

Considering the region outside the green area of Figure 1a, close to the CsPbI_3 ($x < 0.22$) and close to CsPbBr_3 ($x > 0.66$), the formation energy of the Frenkel pair is positive, i.e., endothermic. If energy is not provided to the alloy, the excess of holes tends to occupy the VBM in a delocalized state, and the Frenkel

pair is unlike to form. Especially for $\text{CsPb}(I_{1-x}\text{Br}_x)_3$ with $x > 0.80$, the formation energy of the Frenkel pair is very large, becoming similar to CsPbBr_3 and indicating a tendency for low Frenkel pair concentration in Br-rich alloys.

Relative stability of iodine and bromine Frenkel pair defects in perovskite alloys: There are two possibilities for Frenkel pair formation in the alloy $\text{CsPb}(I_{1-x}\text{Br}_x)_3$: $V_{\text{Br}} + \text{Br}_i$ and $V_1 + I_1$. In contrast to the parent compounds, the local chemical environment of halogen vacancy and halogen interstitial can play an important role in the Frenkel pair relative stability. Before commenting about that, it is important to mention that independent of the local chemical environment, only the 2+ charge states can stabilize the Frenkel pair. In other words, the neutral and 1+ charge state promote the cancelation of the Frenkel pair in the alloy (halogen interstitial move towards the halogen vacancy) as mentioned in the parent's compounds. Translating to the language of experimental results, the Frenkel pair can be observed only in alloys with hole-rich conditions.

Considering the local chemical environment for the halogen interstitial, which is one defect that composes the FP, there are four possibilities in HP alloys: trimers of I (I-I-I), trimers of Br (Br-Br-Br), or multiple compositions as Br-Br-I or I-I-Br. For $\text{CsPb}(I_{1-x}\text{Br}_x)_3$ with $x = 0.5$, the Frenkel pair composed by I trimers is largely stable when compared to trimers of Br, around 0.95 eV. Similarly, I trimers can be at least 0.21 eV more stable than multiple sites as I-I-Br. This is indicative that the Frenkel pair, that has the halogen interstitial composed of Br, is less favorable than the I in alloys, as observed in the alloy parent's compounds.

The halogen vacancy that composes the Frenkel pair could be created in a different local chemical environment, that represents an I-rich or Br-rich, i.e., the vacancy created in the octahedral most composed by I or Br, respectively. The relative stability of the Frenkel pair where the V_1 is created in I-rich can be more than 0.35 eV stable when compared to Frenkel pair with V_1 created in Br-rich $\text{CsPb}(I_{1-x}\text{Br}_x)_3$ with $x = 0.5$.

Our conclusion, owing to the relative stability between the Frenkel pairs is: there is a larger tendency to create $(V_1+I_1)^{2+}$ where the local chemical environment for I_1 is a trimer of I, and the local chemical environment of V_1 is rich in I atoms independently of the alloy composition x . It means that the Frenkel pair will form in regions that are rich (poor) in I (Br). This is expected since the formation of Frenkel pair in CsPbI_3 is much more likely to occur than in CsPbBr_3 as demonstrated before. From this point to the end of this paper, when we mention associated Frenkel pair in the alloy section, we refer to a Frenkel pair that obeys the said characteristics, (V_1+I_1) , and is in the 2+ charge state.

Associated vs. dissociated Frenkel pair in the alloy: In this stage, we check the possibility of dissociation Frenkel pair $(V_1+I_1)^{2+}$ into its defect composition: I_1^{1+} and V_1^{1+} . In Figure 1a, in the red line, we plot the sum of the formation energy of I_1^{1+} and V_1^{1+} (quantity independent of the halogen chemical potential) calculated in the same sites of Frenkel pair defects and E_F at VBM. The difference between the formation energy of the Frenkel pair (blue line Figure 1b) and the dissociated defects (red line Figure 1b) is called binding energy (ΔE), given by Eq. 2 in the Technical Details, and shown in Figure 4. The red area ($\Delta E > 0$) indicates the region where there is a tendency for Frenkel pair

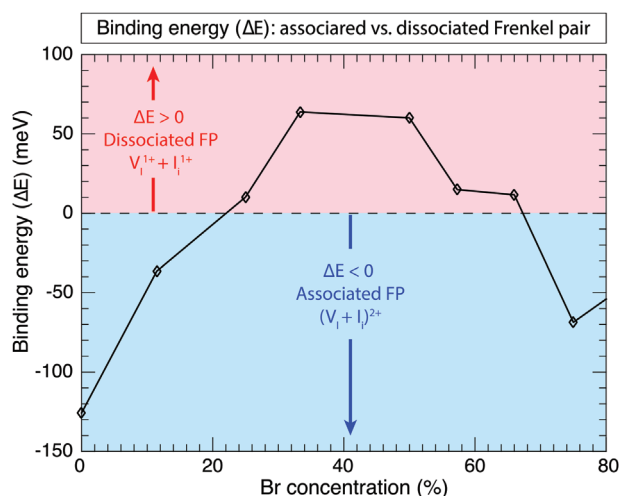


Figure 4. Binding energy for Frenkel pair calculated according to Eq. 2 (Technical Details) for $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ in different Br concentrations. The red area ($\Delta E > 0$) indicates the Br concentration where the Frenkel pair tends to dissociate into their component's defects. The blue area ($\Delta E < 0$) indicates the Br concentration where the FP tends to keep associated.

dissociation, while the blue region ($\Delta E < 0$) refers to the alloy composition that tends to keep an associated Frenkel pair defect format.

For the alloy $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ with composition $0.22 < x < 0.70$ the binding energy is positive, and therefore, whenever the Frenkel pair is formed it will split into I_i^{1+} and V_i^{1+} . The maximum tendency for Frenkel pair dissociation is closer to alloy composition with $0.33 < x < 0.50$, i.e., CsPbI_2Br and $\text{CsPbI}_{1.5}\text{Br}_{1.5}$. The binding energy for $x > 0.70$ and $x < 0.22$ is positive, indicating that, when the Frenkel pair is formed, it tends to keep I_i^{1+} and V_i^{1+} associated.

In summary, considering the three stages described above for alloys of halide perovskite, we have:

- i. the Frenkel pair in alloys can be formed only in the hole-rich condition (under light or hole injection), with a larger preference to show up in the I-rich region inside the alloy.
- ii. For an alloy composition with $0.22 < x < 0.66$, the Frenkel pair has negative formation energy, and the holes tend to localize in the Frenkel pair defect.
- iii. For alloy composition with $0.22 < x < 0.70$, the Frenkel pair tends to dissociate into their composing defects.

2.3. Phase Segregation Mechanism in Halide Perovskites Alloy: $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$

Using the three stages for alloys and their parents' compounds mentioned before, we can describe a mechanism for phase segregation in alloys of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ that is summarized in **Figure 5**. Note that our explanation does not involve thermodynamic properties, but only analysis of defects. Starting from the alloy, **Figure 5a**, the holes can be generated in the HP by light or electrochemically, making the HP in a hole rich condition. In principle, the holes are delocalized at the VBM, as shown by

Figure 5b. However, when the Fermi level of the alloy moves from the middle of the band gap towards the valence band, the formation energy of Frenkel pair $(\text{V}_i + \text{I}_i)^{2+}$ becomes negative for alloys with Br concentration between 22% and 66% and the Frenkel pair defect tends to form spontaneously. This is the driving force that determine the threshold of Br concentration in the alloy. The Frenkel pair is shown in **Figure 5c**. However, in the same range of alloy composition, the Frenkel pair tends to dissociate i.e., the I_i^{1+} and V_i^{1+} move in the opposite direction, **Figure 5d,e**. The dissociation process is caused by the energy gain in the system. In intermediate concentrations of Br, we can say that the associated FP is a metastable configuration (**Figure 1b**) despite being more stable than 2 holes at the valence band. Therefore, under a hole rich condition, the FP tends to form spontaneously by localization of 2 holes in the valence band. The faster migration of iodine over bromine interstitial into the vacant iodine is reflected in the information from the previous calculations of iodine migration.^[22] Also, the experimental results reported by Kamat et al.,^[11,15,19,23] established that the iodine atoms have lower energy barrier to move instead Br atoms. This is a consequence of the higher affinity of Pb and Br when compared to Pb and I.^[15,37] Thus, the I that composes the octahedra around the V_i (not the I that composes the Frenkel pair), moves towards the vacancy. This process creates a region rich in I, **Figure 5f**, and another region with I depletion (large concentration of vacancies and Br) **Figure 5g**. The creation of Frenkel pair and the dissociation will be suppressed only when the **local** chemical environment becomes similar to the **average** alloy concentration with $x < 0.22$ and $x > 0.66$. In both conditions, the holes will not localize anymore in the Frenkel pair and the segregation will stop.

In the dark, and under annealing temperature, the entropy of the system increases, and the ions tend to move. At the same time, the hole-rich condition is suppressed, and the Fermi level of the alloy tends to return to the middle of the band gap. This process decreases the formation energy of the Frenkel pair and isolated V_i and I_i . As a consequence, the I_i tends to fill the V_i , both defects created under light, as shown in **Figure 5i**. Finally, this process recovers the alloy, **Figure 5a**.

Note that our explanation does not invoke pre-existent defects in the HPs alloys. The light (or the excess of holes) is responsible to create the defects as a cascade effect: holes at the VB localize in the form of Frenkel pair and in sequence, the Frenkel pair dissociates. This is observed only in the $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ with $0.22 < x < 0.66$.

2.4. The Effects of Pressure and Alternatives to Suppress the Phase Segregation in Alloys of Halide Perovskite

When creating an alloy of perovskites, a few different effects might take place. Among them, we can cite changes in chemical composition and changes in volume.^[6] The changes in chemical composition for our model were discussed in the previous sections of this paper. Now we discuss the effects of changing the volume to it.

It was demonstrated that the Frenkel pair and isolated V_i and I_i can have negative formation energy when $0.22 < x < 0.66$. This low formation energy could be, in principle, addressed to the volume shrink occasioned by the increase of Br atoms and

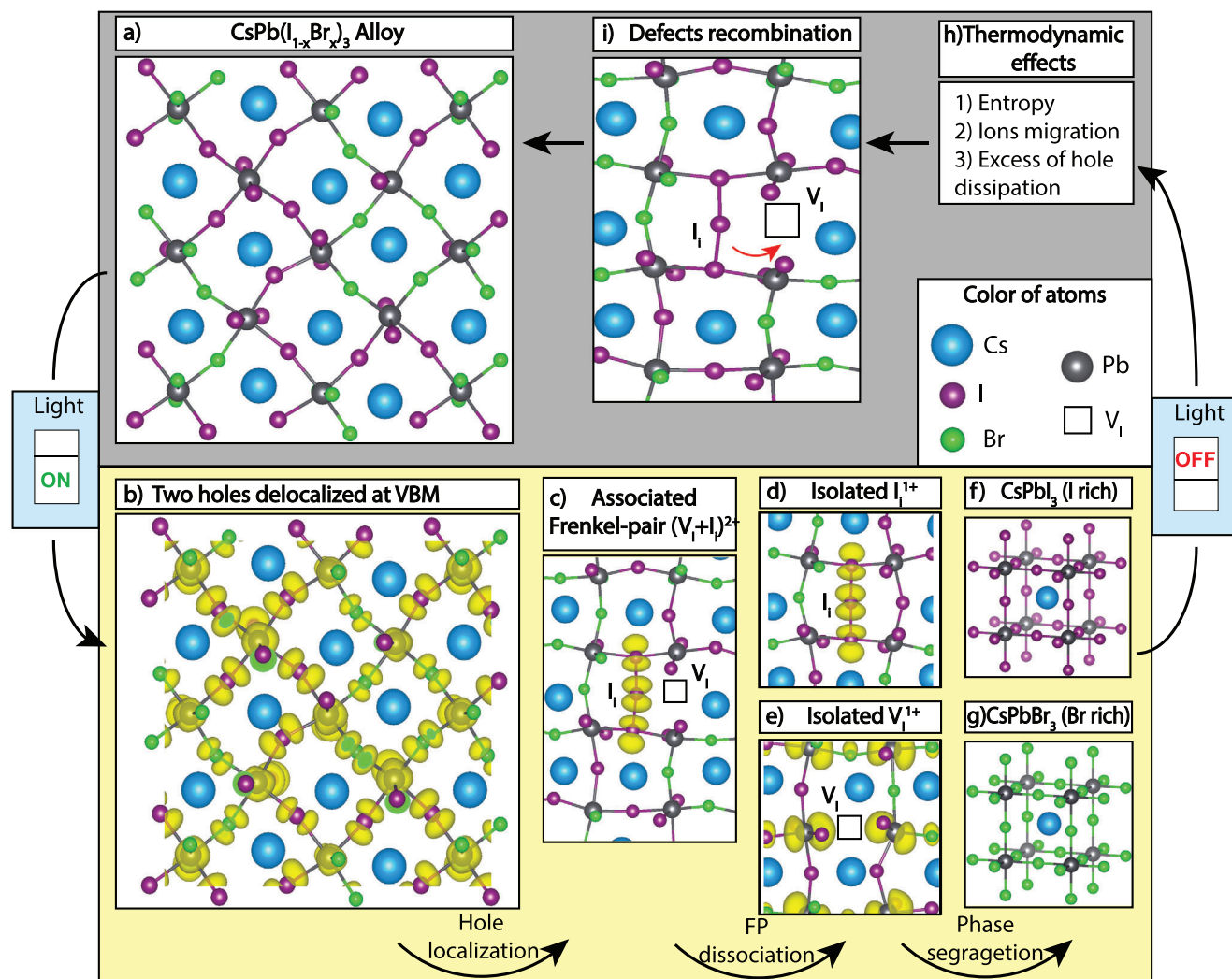


Figure 5. Mechanism for phase segregation. a) Atomistic Representation of the alloy of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ (Cs – blue; Pb– gray; I – purple and Br – green). b) Charge isosurface for two holes delocalized at the valence band maximum of the alloy. c) Charge isosurface for Frenkel pair (associated) defect state $(\text{V}_1+\text{I}_1)^{2+}$ when the two holes at the VBM localize. d) and e) Charge isosurface for isolated (dissociated FP) I_1^+ and V_1^+ , respectively. f) and g) phase segregated into I and Br rich, respectively. h) thermodynamic parameters when the system is under annealing temperature. i) Defects recombination due to the instability of V_1 and I_1 under low hole concentration.

added to our calculation according to Vegard’s law (more details about the calculations are described in the Technical Details). To check the volume effect in the Frenkel pair formation energy, we calculated the Frenkel pair formation energy in the CsPbI_3 under lattice contraction of 2%. We observe that the formation energy of the Frenkel pair increases from 12 meV (no pressure) to 525 meV under high pressure, which corresponds to an increase of 44 times.

This increase in the formation energy of Frenkel pair is expected since this defect is associated with a combination of: energy gain due to atomic rearrangement and energy loss due to the coulomb repulsion between two holes. When the system is under pressure, the coulomb repulsion is larger; at the same time, the volume for the atomic rearrangement is smaller leading to an increase in the formation energy of the Frenkel pair. Therefore, we can say that the volume contraction, due to the alloying composition, is not the driving mechanism to make the for-

mation energy of Frenkel pair negative in the alloys. The presence of the Br atoms in the system must decrease the formation energy of the Frenkel pair. On the other hand, the pressure applied in alloys of halide perovskites can reduce the formation energy of Frenkel pair defects, being a possible path to avoid phase segregation.

Other possibilities to decrease the phase segregation invoke alloying in the A and B sites of perovskites. A-site alloying is the mainstream trend to suppress phase segregation and prepare high-efficiency devices. We expect that since A site atoms/molecules do not contribute significantly to the wavefunction of the valence band maximum or conduction band minimum band edge states, mixing different A site objects will not affect much the electronic structure near the band gap, but might affect the volume. The previous analysis done in pressure in halide perovskite is indirectly related to a mixing of A elements/molecules. The stability of Frenkel pair is related to a

competition of energy gain due to the atomic rearrangement and energy loss due to high coulomb repulsion. The pressure, or the A site mixing, changes the balance between this competition. Our study does not involve different A site alloying simultaneously with X-site alloying. The treatment of double A site substitution complex alloys could create difficulty in isolating some effects and understanding the real reason for the phase segregation.

To test the effect of replacing Pb with Sn at B site on the light induced phase separation through the Frenkel pair defect, we have calculated the Frenkel pair formation in the systems based on Sn rather than Pb, such as CsSnI₃. We find out that even in the 2+ charge state of Sn, the I_i moves towards the vacancy filling it, thus the formation of Frenkel defect is unstable and inhibit phase separation. This process is similar to the Frenkel pair defect in neutral and 1+ charge state for CsPbI₃. For the alloy Cs(Sn_yPb_{1-y})(I_xBr_{1-x}) with [x = 0.50; y = 0.03] we found a metastable state where the FP forms, however its formation energy is 0.32 eV higher than the two holes at the VBM. This means that, the incorporation of Sn always leads to holes being delocalized at the VBM instead of being localized in the Frenkel pair form as in alloys of Pb-based alloys. These results agree with experimental data shown in the literature.^[13]

3. Conclusions

In this paper, we demonstrated that a complex defect composed by iodine interstitial and vacancy of iodine, Frenkel pair (V_i+I_i)²⁺, can have very low formation energy in alloys of CsPb(I_{1-x}Br_x)₃ and be the driven mechanism for phase segregation into its parent compounds under light exposure. The light creates a hole-rich halide perovskite, where the holes tend to localize in the Frenkel pair defect. For Br concentration between 22% and 66%, the Frenkel pair tends to dissociate into V_i¹⁺ and I_i¹⁺. The V_i has a low energy barrier to migrate and is filled by another I, increasing the concentration of I in the region of Frenkel pair formation, and decreasing the concentration of I, where the V_i is moving. The Frenkel pair tends to be created only in the local environment rich in I, which will result in a larger (smaller) concentration of I (Br) until the formation energy of the Frenkel pair becomes positive (holes tend to go to the VBM) or the formation energy of dissociated defects be larger than the Frenkel pair. This process is summarized in Figure 5.

4. Technical Details

A. Computational Technical Details

Our first-principles calculations are based on the density functional theory (DFT) approach as implemented in the Vienna ab-initio simulation package (VASP).^[26,27] The interaction between valence electrons and the ionic cores is treated according to the projected augmented wave method (PAW) method,^[38,39] considering the following valence electrons: Cs (5s²5p⁶6s¹), Pb (6s²6p²), I (5s²5p⁵), Br (4s²4p⁵).

The volume and the atomic positions were optimized with the semi-local exchange and correlation function implemented for solids by Perdew-Burke-Ernzerhof (PBEsol).^[28] We used a plane wave cutoff energy of 400 eV to minimize the stress tensor and

atomic forces with a k-point mesh of 6×6×6 for the Brillouin zone integration. We obtained a lattice parameter of 6.27 Å (6.29 Å) and 5.89 Å (5.85 Å) to CsPbI₃ and CsPbBr₃, which deviate by only -0.32% and 0.68% when compared to experimental results (shown in parentheses), respectively.^[40,41]

To calculate the Frenkel pair and other defects, we used a supercell that corresponds to 2√2x2√2x4 repetitions of Pm-3m cubic perovskites, which contain 32 ABX₃ formula units (160 atoms). In this structure we allowed atomic relaxation keeping frozen the lattice vectors to result in the cubic polymorphous configuration,^[31] which better represents the cubic high symmetry Pm-3m perovskite. Because of the size of the supercell, we reduced the Brillouin zone integration to only the Gamma-point.

In the supercell, we also calculate the electronic and defects properties using the hybrid exchange and correlation functional implemented by Heyd-Scuseria-Ernzerhof (HSE) in addition to the relativistic spin-orbit coupling (SOC) correction.^[29,30] In the standard HSE06, 25% of the exact exchange is included in the short-range region that is defined by the screening factor ω = 0.20 Å⁻¹. However, HSE06+SOC still underestimates the band gap, and therefore to improve the description of the band gap we increase the exact exchange concentration to 43%. This leads to a theoretical band gap of 1.74 eV (1.74 eV) and 2.32 eV (2.23 eV) for CsPbI₃ and CsPbBr₃, in good agreement with the cubic perovskite experimental band gaps shown in parentheses.^[42,43]

To distribute the I and Br atoms in the supercell of alloys CsPb(I_{1-x}Br_x)₃, we used the special quasi-random (SQS) method.^[44,45] The concentration of Br was allowed to vary in the range 0.0 < x < 1.0. The lattice parameter for the alloy was determined by a linear interpolation according to the halogen concentration, using the parents' lattice parameters, i.e., we follow Vegard's law.

B. Defects and formation energy

The formation energy of defects is calculated according to the following equation:

$$\Delta H_f(D, q) = E_{\text{tot}}(D, q) - E_{\text{tot}}^{\text{bulk}} \pm \sum_i n_i \mu_i + qE_F + \Delta^q \quad (1)$$

where $E_{\text{tot}}(D, q)$ is the total energy for the system with defect D in charge state q , $E_{\text{tot}}^{\text{bulk}}$ is the total energy for the bulk system in the same supercell size that contains a defect. The charge state refers to the charge of an ionized defect or valence band, i.e., is associated with the calculation with the addition or removal of electrons. In the case of Frenkel-pair, we remove 1 or 2 electrons from the defect state and, as a consequence, the empty states move toward the conduction band, as demonstrated by the density of states in Figure 3. The number of atoms with chemical specie i that are removed (negative) or added (positive) to the system is indicated by n , and μ_i is the reservoir chemical potential of those atoms n . The Fermi energy, E_F , has the valence band maximum (for alloys and parent compounds) as a reference, set as 0 eV, and can vary between the valence band maximum (VBM) to the conduction band minimum (CBM). Because of the periodic boundary conditions, we need to add a correction in Eq. 1, Δ^q , for the charge image interaction.^[46,47]

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The Frenkel pair defect is composed of one vacancy of halogen and one halogen interstitial – $V_{\text{I}}+I_i$ or $V_{\text{Br}}+Br_i$ - i.e., the supercell that contains the defect is in a stoichiometric condition. Because of that, the formation energy, given by Eq. 1, will be independent of the halogen chemical potential. The same independence of halogen chemical potential occurs when the formation energy of V_{I} and I_i , treated as separate defects, is summed. This is an approach used to avoid the calculation of a stability triangle, which is a hard task to determine the competitive phases of the alloy in different halogen concentrations.

In Eq. 1, we only calculate the formation energy of interesting defects at the valence band maximum, which means, consider $E_F = 0$. This is the strategy to simulate the HPs under the hole-rich condition that is observed experimentally when the alloy goes to phase segregation.^[11,19,23] As mentioned before, the electrons are removed from the alloy by contact with the Fermi level lower than the conduction band minimum, resulting in a shift in the alloy Fermi level towards the valence band maximum.

With the formation energy calculation for the Frenkel pair ($V_{\text{I}}+I_i$ or $V_{\text{Br}}+Br_i$) and the isolated component defects, it is possible to define the binding energy through the following equation:

$$\Delta E = \Delta H_f^{\text{Frenkel}} - \sum_i \Delta H_f^{\text{def}} \quad (2)$$

where $\Delta H_f^{\text{Frenkel}}$ is the formation energy of the Frenkel pair and $\sum_i \Delta H_f^{\text{def}}$ is the sum of the formation energy of isolated defects (halogen interstitial and halogen vacancy – positive charge state). Note that, both quantities are independent of the halogen chemical potential. If $\Delta E < 0$ the formation of Frenkel pair is more stable than the separated defects, which indicates a tendency for halogen vacancy and halogen interstitial stick together. On the other hand, if $\Delta E > 0$ there is a tendency for dissociation of Frenkel pair, and the halogen vacancy and halogen interstitial tend to lie far away from each other.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Allays of halide perovskite, Frenkel pair, Phase segregation

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