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Stabilizing Lead-Free All-Inorganic Tin Halide Perovskites by Ion Exchange

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Supporting Information

ABSTRACT: Because of its thermal stability, lead-free composition, and nearly ideal optical and electronic properties, the orthorhombic CsSnI₃ perovskite is considered promising as a light absorbent for lead-free all-inorganic perovskite solar cells. However, the susceptibility of this three-dimensional perovskite toward oxidation in air has limited the development of solar cells based on this material. Here, we report the findings of a computational study which identifies promising Rb-Cs-Sn(Br-I)₃ perovskites for solar cell applications, prepared by substituting cations (Rb for Cs) and anions (Br for I) in CsSnI₃. We show the evolution of the material electronic structure as well as its thermal and structural stabilities upon gradual substitution. Importantly, we demonstrate how the unwanted yellow phase can be suppressed by substituting Br for I in CsSn(BrIₓ)ₓ with x ≥ 1/3. We predict that substitution of Rb for Cs results in a strongly homogeneous solid solution and therefore an improved film quality and applicability in solar cell devices.

INTRODUCTION

Organic–inorganic hybrid halide perovskite solar cells (PSCs) have attracted strong attention in the past few years and are becoming one of the most promising types of emerging thin-film solar cells. In less than a decade, the power conversion efficiency (PCE) of PSCs has increased from 3.8% in 2009 to 22.7% in 2017. Despite the high efficiency of PSCs, two challenges currently hinder their upscaling toward practical applications. One issue is the long-term instability of PSCs, which is mainly caused by the intrinsic thermal instability of hybrid perovskite materials. Encouragingly, it has been demonstrated recently that mixing the cations or replacing the organic cation with an inorganic cation can improve thermal stability and photostability (e.g., substituting FA for MA in MAPbI₃, Rb for Cs in CsSnI₃, and Cs for MA in MAPbI₃; MA stands for CH₃NH₃, and FA stands for NH₂CHNH₂). The other concern is the well-documented toxicity of lead (Pb), which is particularly problematic because lead halide perovskites decompose into lead compounds that have significant solubility in water. Consequently, an intensive research effort focused on finding air-stable lead-free perovskites suitable as the light-harvesting semiconductor in PSCs is now underway.

Among the various alternatives to lead, tin (Sn) is regarded as a promising substitute because Sn-based hybrid perovskites have been shown to exhibit outstanding electrical and optical properties, including high charge carrier mobilities, high absorption coefficients, and low exciton binding energies. Theoretical predictions by Even et al. and Chiarella et al. also confirmed the promising properties of Sn perovskites, such as suitable band gaps and favorable effective mass. However, Sn-based perovskites also have drawbacks, which have limited their application in efficient PSCs. The primary challenge is the susceptibility of tin toward oxidation from the +2 to the +4 oxidation state upon exposure to ambient air, which, in the case of CsSnI₃, ultimately results in the formation of CsSnIₓ whose relatively weak light absorption across the visible spectrum is undesirable for a photoabsorber. Consequently, to date, there has been much less research effort directed at the advancement of tin halide PSCs than their lead analogues, and their PCE has remained below 10%. Recently, a PCE as high as 9.0% in PSCs was achieved using single-crystalline FASnI₃, made by mixing a small amount of two-dimensional (2D) Sn perovskites with three-dimensional (3D) FASnI₃ in which the organic FA molecules are oriented randomly, an approach that promises further improvement. As compared to hybrid organic–inorganic Sn perovskites, all-inorganic Sn perovskites could have the advantage of...
Marshall et al. achieved the highest PCE to date of 3.56%, used CsSnI₃ to fabricate a Schottky contact solar cell, which variation of perovskites are scarce. There have been a few attempts to fabricate solar cells using CsSnI₃ as a photoactive layer, but their maximum efficiency was still low. In 2012, Chen et al. first used CsSnI₃ to fabricate a Schottky contact solar cell, which achieved a PCE of 0.9%. In 2014, Kumar et al. achieved a PCE of 2.02% by forming the perovskite from a solution under illumination without device encapsulation. However, the PCE to our knowledge, the amalgamated relative stability of the structures as compared to the Y phase shows the crystal structures and cells used in the DFT implementation in the Vienna ab initio simulation package (VASP). The Perdew, Burke, and Ernzerhof (PBE) functional within the generalized gradient approximation is used. The outermost s, p, and d (in the case of Sn) electrons are treated as valence electrons, whose interactions with the remaining ions are modeled by pseudopotentials generated over the lower open-circuit voltage. The most important challenges are therefore to develop ways to increase the open-circuit voltage and to stabilize tin halide perovskites toward oxidation in air. The oxidation instability manifests as a phase transition from the photoactive black orthorhombic phase to a photoinactive 2D yellow phase upon exposure to water vapor, which spontaneously converts to the weakly absorbing one-dimensional Cs₂SnI₆ leading to difficulties in controlling the morphology and quality of the perovskite film.

In Pb halide perovskites, the strategy of mixing cations or anions has been widely used to improve the stability and PV performance of PSCs. In contrast, explorations of the mixing of cations and anions in all-inorganic Sn-based perovskites are scarce. Recently, the electronic structure variation of CsSnI₃ by mixing A-site cations (e.g., mixing Cs and Rb) has been investigated by Jung et al. However, the relative stability of the structures as compared to the Y phase was not investigated. To our knowledge, the amalgamated effect of exchange of both the A-site metal cation and the halide anion in completely inorganic tin perovskites has not been investigated.

In this paper, we present a theoretical study of the impact of cation and anion mixing (Rb/Cs cation exchange and Br/I anion exchange) in all-organic γ-CsSnI₃ using the density functional theory (DFT)-1/2 method [the local density approximation (LDA)-1/2 version] taking into account the spin–orbit coupling (SOC) effect. We focus on the evolution of the electronic properties as well as the thermal and structural stabilities when substituting Br for I and Rb for Cs in γ-CsSnI₃. We predict that 3D perovskites with the composition RbₓCs₁₋ₓSn(Br₁₋ₓIₓ)₃, where 0 ≤ x, y ≤ 1, are direct band gap semiconductors with band gaps in the range 1.3–2.0 eV. Importantly, our results indicate that substitution of Br for I in CsSnI₃ can prevent the unwanted γ-to-Y phase transition, evidenced by the favorable formation energies of the γ phase over the Y phase. In addition, calculations of the free energy of mixing and the prediction of phase diagram demonstrate that further substitution of Rb for Cs in CsSn(Br₁₋ₓIₓ) can improve the mixing thermodynamics, which is expected to improve the film-forming properties. Our predicted trends in the thermodynamic stability and band gaps provide a guideline to develop more efficient and stable lead-free all-inorganic perovskites for PSCs.

**COMPUTATIONAL METHODS AND STRUCTURAL MODELS**

The initial structure optimizations are performed using DFT as implemented in the Vienna ab initio simulation package (VASP). The Perdew, Burke, and Ernzerhof (PBE) functional within the generalized gradient approximation is used. The outermost s, p, and d (in the case of Sn) electrons are treated as valence electrons, whose interactions with the remaining ions are modeled by pseudopotentials generated within the projector-augmented wave method. The crystal structures and cells used in the DFT calculations. Unit cells with 20 atoms (four ASnX₃ units) are used for all structures using a 1 × 1 × 1 cell for the γ and Y phases and 2 × 2 × 1 supercells for the α phase. In the structural optimization, the positions of the atoms as well as the cell volume and cell shape are all allowed to relax by setting...
ISIF = 3. An energy cutoff of 500 eV and 4 × 4 × 8, 6 × 4 × 6, and 4 × 10 × 2 k-point meshes (α, γ, and Y phase structures, respectively) are used to achieve an energy and force convergence of 0.1 meV and 2 meV/Å, respectively. The subsequent electronic structure calculations were performed using an efficient approximate quasi-particle DFT method, namely, the DFT-1/2 method. The DFT-1/2 method stems from Slater’s proposal of an approximation for the excitation energy, a transition-state method, to reduce the band gap from Slater’s approximation. Recently, we successfully applied this method in predicting accurate band gaps of metal halide perovskites. The computational effort is the same as for standard DFT, with a straightforward inclusion of SOC when coupled with VASP. In this work, we extend the use of the DFT-1/2 method with the same settings (CUT values of 0.1%). It should be noted here that the predicted lattice parameters of α-CSnI3 and γ-CSnI3 in our previous work are smaller because of the use of LDA, which slightly underestimates the lattice parameters. In this work, PBE is used, resulting in a slight overestimation of lattice parameters. Consequently, the predicted band gap of γ-CSnI3 (1.36 eV) in this work (will be discussed in the next paragraph) is slightly higher compared to that of previous work (1.34 eV).

The calculated band gaps of γ-CSnI3 and γ-CSnBr3 are 1.36 and 1.72 eV, respectively, in excellent agreement with reported experimental measurements (1.27 and 1.75 eV) and GW0 calculations (1.34 and 1.83 eV). There are no experimental reports known to us of the band gap of either RbSnI3 or RbSnBr3. Only theoretical results from HSE06 for γ-RbSnI3 and PBE for α-RbSnBr3 are found to be 1.41 and 0.57 eV, respectively. Our predicted band gap for RbSnI3 is slightly underestimated.

The calculated band gap of γ-CsSnI3 (1.36 eV) would be the fundamental limit according to the formula

$$\Delta E = -k_B T \ln \frac{\gamma}{\Delta H}$$

where $\Delta E$ is the band gap, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. The internal energy of mixing of Rs-CsSnX3 is then calculated using the formula

$$\Delta U = E_{Rs-CsSnX3} - xE_{RbSnX3} - (1 - x)E_{CsSnX3}$$

where $E_{Rs-CsSnX3}$, $E_{RbSnX3}$, and $E_{CsSnX3}$ are the total energies of Rs-CsSnI3, RsSnI3, and CsSnI3, respectively. The entropy of mixing of Asn(BrI1-3) is calculated using the formula

$$\Delta S = -k_B \ln \frac{\gamma}{\Delta H}$$

The critical temperature for mixing and into the stability of the solid solution for typical temperatures at which perovskites are synthesized.

Table 1. Lattice Constants (in Å) Obtained by DFT and Band Gap Energies $E_g$ (in eV) Obtained with the DFT-1/2 Method Including SOC Compared to Experimental Data and Theoretical Predictions Based on Hybrid and GW Methods

<table>
<thead>
<tr>
<th>material</th>
<th>lattice constants (this work)</th>
<th>lattice constants (experimental)</th>
<th>lattice constants (other theoretical work)</th>
<th>$E_g$ (DFT-1/2 + SOC)</th>
<th>$E_g$ (HSE06)</th>
<th>$E_g$ (GW0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-CsSnI3</td>
<td>8.69, 12.38, 8.63</td>
<td>8.62, 12.38, 8.64</td>
<td>8.94, 12.52, 8.60</td>
<td>1.36</td>
<td>1.27</td>
<td>1.34</td>
</tr>
<tr>
<td>γ-RbSnI3</td>
<td>8.91, 12.28, 8.47</td>
<td>8.93, 12.28, 8.47</td>
<td>9.31</td>
<td>1.55</td>
<td>1.13</td>
<td>1.15</td>
</tr>
<tr>
<td>γ-CsSnBr3</td>
<td>8.36, 11.79, 8.22</td>
<td></td>
<td>8.38</td>
<td>1.72</td>
<td>1.13</td>
<td>1.15</td>
</tr>
<tr>
<td>γ-RbSnBr3</td>
<td>8.38, 11.55, 7.98</td>
<td></td>
<td>8.38</td>
<td>2.01</td>
<td>1.13</td>
<td>1.15</td>
</tr>
</tbody>
</table>


RESULTS AND DISCUSSION

Before studying the mixing of A cations and X anions in AsnX3, we first performed calculations for the four pure compounds: CsSnI3, CsSnBr3, RbSnI3, and RbSnBr3. The calculated lattice parameters of orthorhombic (γ) AsnX3 are shown in Table 1. Those of other polymorphs including cubic α, tetragonal β, and Y phase structures are listed in Table S2. The optimized lattice parameters are in good agreement with experiments, with a slight overestimation of lattice constants by about 1%, and with other theoretical results (differences within 0.1%) . It should be noted here that the predicted lattice parameters of α-CsSnI3 and γ-CsSnI3 in our previous work are smaller because of the use of LDA, which slightly underestimates the lattice parameters. In this work, PBE is used, resulting in a slight overestimation of lattice parameters. Consequently, the predicted band gap of γ-CsSnI3 (1.36 eV) in this work (will be discussed in the next paragraph) is slightly higher compared to that of previous work (1.34 eV).

The calculated band gaps of γ-CsSnI3 and γ-CsSnBr3 are 1.36 and 1.72 eV, respectively, in excellent agreement with reported experimental measurements (1.27 and 1.75 eV) and GW0 calculations (1.34 and 1.83 eV). There are no experimental reports known to us of the band gap of either RbSnI3 or RbSnBr3. Only theoretical results from HSE06 for γ-RbSnI3 and PBE for α-RbSnBr3 are found to be 1.41 and 0.57 eV, respectively. Our predicted band gap for γ-RbSnI3 is 1.55 eV. Substituting Br for I in γ-RbSnI3 further increases the band gap to 2.01 eV.

It is worth noting that although CsSnBr3 is reported to have the α structure at room temperature, the actual atomic arrangement at finite temperature (due to the dynamic...
In general, the band gap increases with increasing percentage of Br in ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} and Rb in Rb\textsubscript{1−x}Cs\textsubscript{x}SnI\textsubscript{3}. From Figure 2a and Table S4, generally, the band gaps change because of the variations in both volume and lattice distortion. However, the changes in cell volume have more pronounced effects on the band gaps than the changes in lattice distortion, that is, octahedral tilting. The reduction of the cell volume is responsible for the widening of the band gap in ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} or Rb\textsubscript{1−x}Cs\textsubscript{x}SnI\textsubscript{3} solid solutions with an increased Br or Rb percentage. For the band gap variations with the same Br or Rb percentage in ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} or Rb\textsubscript{1−x}Cs\textsubscript{x}SnI\textsubscript{3} solid solutions, there is no certain relationship found between the degree of lattice distortion (i.e., the degree of octahedral tilting, which is the tilting angle difference $\Delta\theta$) and band gaps.

It is well-known that for single-junction and multijunction solar cells, the Shockley–Queisser limit suggests that the power conversion efficiency (PCE) cannot exceed a maximum of 31%. The band gaps of CsSn\textsubscript{3}, RbSn\textsubscript{3}, and RbSnI\textsubscript{3} are almost completely in the optimal range (1.30–1.55 eV) for single-junction PSCs. When substituting Rb for Cs in CsSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3}, the band gaps of RbSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} increase by 0.2–0.3 eV as compared to their Cs counterparts, making RbSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} ($x > 1/3$) ideal as a wide-band gap material for tandem solar cells in conjunction with narrow-band gap semiconductors such as Si or CsSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3}. The changes in band gap when mixing Rb and Cs cations are much smaller than those when mixing I and Br. This is true for all values $0 \leq y \leq 1$ and also for different structures with a fixed y. The band gaps of Rb\textsubscript{1−x}Cs\textsubscript{x}SnBr\textsubscript{3} (1.71–2.01 eV) and Rb\textsubscript{1−x}Cs\textsubscript{x}SnI\textsubscript{3} (1.36–1.55 eV) are in the ideal range for tandem and single-junction solar cells, respectively.

In addition to the band gap, another key property for the application of mixed inorganic perovskites in PSCs is their structural stability. CsSnI\textsubscript{3} has two coexisting polymorphs (the $\gamma$ and Y phases) at room temperature, which both belong to the $Pnma$ space group. Although both phases have similar free energies and stable phonon modes, a transition from the black $\gamma$ phase to the yellow Y phase has been observed in ambient conditions. Oxidation of Sn\textsuperscript{2+} to Sn\textsuperscript{4+} spontaneously occurs after the transformation of the $\gamma$ phase to the Y phase. Because of the different crystal structure and electronic properties of the Y phase (i.e., a 2D structure and an indirect band gap of 2.6 eV), the unwanted phase transition from $\gamma$ to Y can considerably decrease the efficiency of a solar cell. In addition, the Y phase will spontaneously react with O\textsubscript{2} when exposed to air, resulting in Cs\textsubscript{2}SnI\textsubscript{6} with a face-centered cubic structure. Therefore, we focus here on the evolution of the stability of the $\gamma$ and Y phases upon gradual substitution of Br for I and Rb for Cs. The results of our calculations for other structures are given in Figure S5.

The formation energy $\Delta H$ of ASnX\textsubscript{3}, AX, and SnX\textsubscript{2} is defined as $\Delta H = E_{\text{ASnX}_3} - E_{\text{AX}} - E_{\text{SnX}_2}$, where $E_{\text{ASnX}_3}$, $E_{\text{AX}}$, and $E_{\text{SnX}_2}$ are the total energies of ASnX\textsubscript{3}, AX, and SnX\textsubscript{2}, respectively. Here, a negative value of $\Delta H$ represents favorable formation of ASnX\textsubscript{3} perovskites.

$\Delta H$ values for the formation of ASnX\textsubscript{3} are negative in most cases, indicating that the formation of ASnX\textsubscript{3} is favorable. The $\Delta H$ values for different substitutions are shown in Figure S6. The $\Delta H$ values for $\gamma$-ASnI\textsubscript{3} and $\gamma$-ASnBr\textsubscript{3} are very close, which indicates that both phases are thermodynamically stable. However, the $\Delta H$ values for RbSnI\textsubscript{3} and RbSnBr\textsubscript{3} are significantly different, indicating that RbSnI\textsubscript{3} is more thermodynamically stable than RbSnBr\textsubscript{3}. As mentioned earlier, the reduction of the cell volume is responsible for the widening of the band gap in ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} or RbSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} solid solutions with an increased Br or Rb percentage. The band gap variations with the same Br or Rb percentage in ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} or RbSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} solid solutions, there is no certain relationship found between the degree of lattice distortion (i.e., the degree of octahedral tilting, which is the tilting angle difference $\Delta\theta$) and band gaps.

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more negative $\Delta H$, the more stable the corresponding structure. It can be clearly seen in Figure 3 that all perovskites considered exhibit good thermal stability, with large negative $\Delta H$ values. Figure 3 also shows the effect of ion mixing on the stability of the $\gamma$ phase with respect to the $Y$ phase.

For CsSn$I_x$, the formation energies of the $\gamma$ and $Y$ phases are the same. However, with the increase of Rb concentration, the structural instability of Rb$_x$Cs$_{1-x}$Sn$I_3$ becomes increasingly pronounced. Consequently, upon exposure to air, the rate at which the perovskite oxidizes is predicated to increase with an increasing Rb concentration. The substitution of Rb for Cs seems to facilitate the formation of the $Y$ phase, as evidenced by the more negative formation energy of the $Y$ phase than the $\gamma$ phase. Indeed, the instability of the $\gamma$ phase is in agreement with the experimental observation of RbSn$I_3$ only existing in a 2D yellow phase. On the contrary, for CsSnBr$_3$, the formation energy of the $Y$ phase is much less negative than that of the $\gamma$ phase (by 0.06 eV), indicating that the $\gamma$ phase is more stable than the $Y$ phase. The substitution of Rb for Cs results in a slight decrease (to 0.04 eV) in the energy difference between the two phases, with the $\gamma$ phase still being favored.

The formation energies of mixing Cs and Rb in Rb$_x$Cs$_{1-x}$Sn$I_3$ or Rb$_x$Cs$_{1-x}$SnBr$_3$ follow a perfect linear relation (Figure 3b), indicating favorable mixing thermodynamics. However, substitution of Br for I (Figure 3a) shows an unusual trend as a function of $x$: the curves show first a decrease and then an increase, with a valley point at $x = 1/3$ in both CsSn(Br$_{1-x}$I$_x$)$_3$ and RbSn(Br$_{1-x}$I$_x$)$_3$. When $x < 1/3$, the most negative $\Delta H$ of the $\gamma$ phase for each concentration is relatively more positive than or nearly equal to the most negative $\Delta H$ of the $Y$ phase, which indicates that the $Y$ phase is favored over the $\gamma$ phase. When $x = 1/3$, the most negative $\Delta H$ of the $\gamma$ phase is clearly more negative than the most negative $\Delta H$ of the $Y$ phase, whereas the least negative $\Delta H$ of the $\gamma$ phase is almost equal to the most negative $\Delta H$ of the $Y$ phase. When $x > 1/3$, all $\Delta H$ of the $\gamma$ phase for each concentration are more negative than those of the $Y$ phase, which means that the $\gamma$ phase is stabilized. For Rb$_x$Cs$_{1-x}$Sn$I_3$ or Rb$_x$Cs$_{1-x}$SnBr$_3$, mixing Cs and Rb does not change the stability of the $Y$ phase with respect to the $\gamma$ phase. However, for Rb$_x$Cs$_{1-x}$Sn$I_3$, the opposite is true. We conclude that the addition of Br to Rb$_x$Cs$_{1-x}$Sn$I_3$ tends to stabilize the favorable $\gamma$ phase and suppress the formation of the $Y$ phase.

Results of these calculations are shown in Figure S6. On the basis of the Helmholtz free energies, we plot the phase diagram for $\gamma$-AsnIX$_y$ by using the GQCA code, as shown in Figure 4. For CsSn(Br$_{1-x}$I$_x$)$_3$, the critical temperature is 291 K (see Figure 4a), indicating that the mixing of anions (I and Br) is favorable at room temperature (300 K). However, for RbSn(Br$_{1-x}$I$_x$)$_3$ at 300 K, a miscibility gap is found in the composition region between $x_1 = 0.33$ and $x_2 = 0.70$ (see Figure 4b). The pure compounds RbSn$I_3$ and RbSnBr$_3$ are not miscible inside the miscibility gap under equilibrium conditions, leading to the formation of two phases with Br concentrations $x_1$ and $x_2$. Meanwhile, the alloy has spinodal points at the compositions $x_1 = 0.40$ and $x_2 = 0.62$ at room temperature. Thus, in the intervals $x_1 < x < x_1'$ and $x_2' > x > x_2$, a metastable phase can occur, showing small fluctuations in composition. The predicted critical temperature (the temperature above which the solid solution is stable for any...
composition) is 312 K, which is significantly lower than the critical temperature of 343 K predicted for the MAPb(Br\textsubscript{x}I\textsubscript{1−x})\textsubscript{3} perovskite.\textsuperscript{63} This indicates that, although mixing of Br and I is not favored slightly below (for Cs\textsubscript{1−y}Sn\textsubscript{y}(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3}) or around (for RbSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3}) room temperature, the phase segregation in these alloys is less significant than that in MAPb(Br\textsubscript{x}I\textsubscript{1−x})\textsubscript{3} perovskites.

A uniform mixture can be synthesized either through control of the deposition kinetics or by annealing above the critical temperature. The uniform mixture tends to segregate below the critical temperature, but this segregation is a very slow process.\textsuperscript{63} The inclusion of smaller cations often provides an improvement, overcoming kinetic barriers and changing the local critical temperature. For example, smaller cations such as Cs and Rb were introduced in (FA/MA)Pb(1/Br)\textsubscript{3} and were shown to have a positive effect on the structural and photostability of state-of-the-art PSCs.\textsuperscript{6,10,13,78} Indeed, we predict that mixing of Rb and Cs in Rb\textsubscript{x}Cs\textsubscript{1−x}SnX\textsubscript{3} is very favorable at room temperature. For Rb\textsubscript{x}Cs\textsubscript{1−x}SnBr\textsubscript{3} and Rb\textsubscript{x}Cs\textsubscript{1−x}SnI\textsubscript{3}, the phase diagrams show that mixing of cations (Rb and Cs) is favorable at temperatures above 118 and 137 K, respectively (see Figure 4c,d). Our prediction of the critical miscibility temperature of 137 K of Rb\textsubscript{x}Cs\textsubscript{1−x}SnI\textsubscript{3} is in good agreement with the result of 140 K calculated by Jung et al.\textsuperscript{7}

The slight difference of the predicted critical temperature could be caused by the small variation in energies per cell due to the differences in computational settings (energy cutoff value, k-point grid, version, and implementation of VASP codes) in DFT calculations. The critical temperatures of mixing of Rb and Cs in Rb\textsubscript{x}Cs\textsubscript{1−x}SnX\textsubscript{3} are much lower than those of mixing of Br and I in ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3}. Therefore, additional mixing of Cs and Rb in ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} is predicted to bring down the critical temperature for mixing of Br and I below room temperature, suppressing phase segregation and resulting in better material quality for PV applications.

**CONCLUSIONS**

In summary, the effects of cation (Cs and Rb) and anion (I and Br) mixing in all-inorganic tin halide perovskites have been investigated with DFT-based calculations. Using standard DFT for structure optimization and the DFT-1/2 method with SOC for band structure calculations, we studied the evolution of the structural, thermodynamic, and electronic properties as a function of substitution of Br for Cs and Br for I. We predict that Cs\textsubscript{x}Rb\textsubscript{1−x}Sn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} perovskites have direct band gaps in the range of 1.3–2.0 eV. The alloys with high I and Cs concentrations are well suited for highly efficient single-junction PSCs, whereas those with high Rb and Br concentrations are suitable as wide-band gap materials for tandem PSCs. Importantly, we found that substitution of Br for I can suppress the unwanted γ-to-Y phase transition. The critical concentration for stabilization of the γ phase with respect to the Y phase in Cs\textsubscript{x}Rb\textsubscript{1−x}Sn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} is \( x = 1/3 \). Furthermore, phase diagrams based on the free energy of mixing show that a solid solution of Br and I is thermodynamically possible around and slightly above room temperature for CsSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} and RbSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3}, respectively. Finally, substitution of Rb for Cs to ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} is predicted to decrease the critical temperature to well below room temperature, enabling the formation of highly homogeneous solid solutions for improved solar cell performance. Our predictions regarding the stabilization of the γ phase and the use of five elements in Rb\textsubscript{x}Cs\textsubscript{1−x}Sn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} as an efficient and stable light absorber for PSCs call for experimental exploration.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b04013.

Physical insights of why Sn p and halide I or Br p orbitals are both half-ionized; illustration of the selection strategy of ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} to reduce computational effort; summary of lattice constants and band gaps (\( E_g \)) of polymorphs of ASnX\textsubscript{3} (CsSn\textsubscript{3}, RbSn\textsubscript{3}, CsSnBr\textsubscript{3}, and RbSnBr\textsubscript{3}); band structures for CsSn\textsubscript{3}, CsSnBr\textsubscript{3}, RbSn\textsubscript{3}, and RbSnBr\textsubscript{3} with the γ phase and the α phase; effective masses for γ-CsSn\textsubscript{3}, γ-CsSnBr\textsubscript{3}, γ-RbSn\textsubscript{3}, and γ-RbSnBr\textsubscript{3}; average tilting angles and cell volumes of γ-CsSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3}, γ-RbSn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3}, γ-Cs\textsubscript{1−y}Sn\textsubscript{y}Br\textsubscript{3}, and γ-Rb\textsubscript{1−y}Cs\textsubscript{y}Sn\textsubscript{3} band gaps and formation energies of ASn(Br\textsubscript{1−x}I\textsubscript{x})\textsubscript{3} and Rb\textsubscript{x}Cs\textsubscript{1−x}SnX\textsubscript{3} perovskites, including the α phase; and Helmholtz free energy of mixing of α and γ polymorphs (PDF)

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