

# Earth-Abundant Nontoxic Titanium(IV)-based Vacancy-Ordered Double Perovskite Halides with Tunable 1.0 to 1.8 eV Bandgaps for **Photovoltaic Applications**

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S Supporting Information

ABSTRACT: The possibility of lead (Pb) contamination and the volatility of the organic cations in the prevailing Pb-based organic-inorganic perovskite (HP) light absorbers are the two key issues of concern in the emerging perovskite solar cells (PSCs). The majority of the Pb-free HP candidates that are being explored for PSCs either suffer from instability issues and have unfavorable defect properties or have unsuitable bandgaps for PSC applications. We report the prediction of a promising new family of allinorganic HPs based on the nontoxic, earth-abundant, ultrastable Ti(IV) for use in PSCs. We show that the Ti-based HPs possess a combination of several desirable attributes, including suitable bandgaps, excellent optical absorption, benign defect properties, and high stability. In particular, we show



experimentally that representative members of the Ti-based HP family,  $Cs_2TiI_xBr_{6-x}$  have bandgaps that can be tuned between the ideal values of 1.38 and 1.78 eV for single-junction and tandem photovoltaic applications, respectively.

alide perovskites (HPs) are a family of semiconductor materials that have shown great promise as light absorbers in the emerging perovskite solar cells (PSCs).<sup>1-4</sup> Owing to the exceptional optoelectronic properties of HPs, the record power conversion efficiency (PCE) of PSCs has surpassed 22% within only a few years.<sup>4</sup> Despite the rapid surge in the record PCE, there are two key issues regarding HP materials that need to be resolved before PSC technology can be widely commercialized. First, the state-of-the-art HP materials in the high-PCE PSCs all contain toxic lead (Pb); the use of Pb in devices is severely restricted in many countries and regions.<sup>5,6</sup> Second, all of the HPs in the highest-performing PSCs contain organic cations, such as formamidinium (FA<sup>+</sup>) or methylammonium (MA<sup>+</sup>),<sup>1,2</sup> which are highly hygroscopic and volatile. This renders the state-of-the-art HPs intrinsically unstable, with inadequate tolerance for environmental (e.g., thermal, moisture) stresses.<sup>7-8</sup> Thus finding all-inorganic Pbfree HPs that can address both issues without sacrificing some of the key properties, for example, bandgaps, optical absorption, and defect tolerance, for PSCs is still a great challenge, although previous efforts in this area have been met with some success.<sup>9,10</sup> It is widely recognized that replacing MA<sup>+</sup> or FA<sup>+</sup> by cesium (Cs<sup>+</sup>) in HPs can significantly enhance their thermal/moisture stability.<sup>11</sup> Also, it has been shown that  $Pb^{2+}$  can be replaced by other cations, such as tin  $(Sn^{2+})$ , 9,10,12germanium  $(Ge^{2+})$ ,<sup>13</sup> bismuth  $(Bi^{3+})$ ,<sup>14</sup> antimony  $(Sb^{3+})$ ,<sup>15</sup> indium (In<sup>+</sup>),<sup>16,17</sup> and silver (Ag<sup>+</sup>).<sup>18-20</sup> It is then natural to combine these two ion-substitution strategies in searching for nontoxic, all-inorganic HPs for PSCs. However, the majority of the recently developed Pb-free, all-inorganic HPs have bandgaps that are not suitable for single-junction or tandem photovoltaic (PV) applications. CsSnI<sub>3</sub> HP with one bandgap of  $\sim$ 1.3 eV is an exception, which is why it has drawn the most attention.<sup>21-23</sup> Despite substantial effort, the development of efficient CsSnI<sub>3</sub>-based PSCs is severely hampered by the metallic conductivity of CsSnI<sub>3</sub> HP.<sup>15,22,23</sup> Furthermore, Sn<sup>2+</sup> is extremely sensitive to moisture and oxygen in the ambient.<sup>21</sup> Thus preventing CsSnI<sub>3</sub> HP from degrading is much more challenging than its Pb-based HP counterparts. Furthermore, there can be a certain level of toxicity in Sn-based HPs, as reported by Babayigit et al.<sup>24</sup> In this context, the compound Cs<sub>2</sub>SnI<sub>6</sub> with a special double-perovskite crystal structure, containing ordered vacancies due to the +4 oxidation state of Sn, has also been proposed as a candidate for use in PSCs.<sup>25</sup>

Received: November 22, 2017 Accepted: December 22, 2017 Published: December 22, 2017



Figure 1. (A) Schematic crystal structure of  $A_2 TiX_6$  HPs. (B) Computed bandgaps of various HPs using HSE06 functional. The range of optimal bandgaps for solar-cell materials is highlighted by the horizontal band. (C) Computed optical absorption spectra (based on the HSE06 functional) of several predicted HPs, compared with absorption spectra of Si and MAPbI<sub>3</sub> HP. The absorption coefficient of MAPbI<sub>3</sub> is computed using the PBE functional without considering the SOC effect. Note that the computed absorption spectrum of MAPbI<sub>3</sub> is coincidentally in good agreement with the experimental spectrum due to the cancellation of errors by using the PBE functional without considering SOC. (D) Computed band structure of  $Cs_2TiI_6$  based on primitive unit cell (Figure S1) using PBE functional; here  $\Gamma$  (0.0, 0.0, 0.0), W (0.5, 0.25, 0.75), L (0.5, 0.5), X (0.5, 0.0, 0.5), and K (0.375, 0.375, 0.75) refer to the high-symmetry special points in the first Brillouin zone. (E) Computed DOS and projected DOS of  $Cs_2TiI_6$  using HSE06 functional.

However,  $Cs_2SnI_6$  is found to exhibit insufficient stability, and it contains intrinsically deep defects that are detrimental to the PSC performance.<sup>26</sup> In fact, many nontoxic transition metals possess stable +4 oxidation state, and thus, there are opportunities for finding new promising HP materials for PSCs by replacing  $Sn^{4+}$  in  $Cs_2SnI_6$  by other transition-metal cations. This is confirmed by a recent study by Sakai et al.<sup>27</sup> who reported  $Cs_2PdBr_6$  as a possible HP for use in PSCs. However,  $Cs_2PdBr_6$ -based PSC has not been demonstrated as yet, and it contains the noble element Pd, making it potentially unaffordable.

In this integrated theoretical and experimental study, we unravel a promising new family of vacancy-ordered halide double perovskites based on the earth-abundant, nontoxic, and ultrastable Ti(IV) for use in PSCs. This HP family has a general chemical formula  $A_2TiX_6$  (A = K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, In<sup>+</sup>, MA<sup>+</sup>, or FA<sup>+</sup>; X = Cl, Br, or I). Our first-principles density functional theory (DFT) calculations show that several materials in this HP family possess desired optical/electronic properties, for example, suitable bandgaps in the range 1.0 to 1.8 eV as well

as tunable defect properties. We have also synthesized experimentally a series of  $Cs_2TiI_xBr_{6-x}$  (x = 0, 2, 4, 6) HPs using the melt-crystallization method.<sup>21</sup> Both theoretical computations and experimental measurements show that the bandgap of  $Cs_2TiI_xBr_{6-x}$  HPs can be tuned continuously from 1.02 to 1.78 eV. In particular,  $Cs_2TiI_2Br_4$  and  $Cs_2TiBr_6$  and HPs exhibit bandgaps of 1.38 and 1.78 eV, which are ideal for application in single-junction PSCs and tandem PVs, respectively. The stability and processability of these newly synthesized HPs are demonstrated, attesting to the promise of their use in PSCs.

Like  $Cs_2SnI_{6}$ , all of the optimized structures of vacancyordered  $A_2BX_6$  HPs considered here are  $K_2PtCl_6$ -type (see Figure 1A).<sup>25,28</sup> The  $A_2BX_6$  HPs may be viewed as a derivative structure of the conventional ABX<sub>3</sub> HPs in which every other  $B^{2+}$  cation is missing. The interrupted solid-state framework results in isolated  $[BX_6]^{2-}$  octahedra and discrete anions, akin to molecular salts.<sup>25</sup> Because the bandgap of the light-absorbing material in PVs is one of the most important properties, the computed bandgaps for all HPs considered here were

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Figure 2. (A) Allowed values of Ti and I chemical potentials (gray shaded region), which define the thermodynamic stability of Cs<sub>2</sub>TiI<sub>6</sub>. The chemical potentials  $\mu_{Ti}$ ,  $\mu_{I_1}$  and  $\mu_{Cs}$  are limited by the formation of the secondary phases CsI<sub>4</sub>, CsI<sub>3</sub>, CsI, TiI<sub>3</sub>, and TiI<sub>4</sub>. The two solid black circles labeled  $\alpha$  and  $\beta$  correspond to the two extreme cases:  $\alpha$  (I-rich/Ti-lean,  $\mu_{Ti} = -3.33$  eV,  $\mu_{I} = -0.035$  eV,  $\mu_{Cs} = -3.61$  eV) and  $\beta$  (I-lean/Ti-rich,  $\mu_{Ti} = 0$  eV,  $\mu_{I} = -1.06$  eV,  $\mu_{Cs} = -2.20$  eV), both selected for calculating the formation energies of a point defect. Computed formation energies of various intrinsic point defects versus the Fermi level in two extreme cases in Cs<sub>2</sub>TiI<sub>6</sub>: (B) I-rich/Ti-lean and (C) I-lean/Ti-rich.

computed (Figure 1B). For the same A-site cation, the bandgap increases gradually in the order I < Br < Cl, which is consistent with the bandgap trend seen in MAPbX<sub>3</sub> (X = I, Br, Cl) HPs.<sup>3</sup> It is also observed that the bandgap of the HPs studied here becomes wider with increasing A-site cation radius, suggesting that the tilting of the  $[BX_6]^{2-}$  octahedron dictated by the A-site cation can markedly affect the electronic structures of these HPs. Note that the bandgap of the HPs can be tuned via substitution of both the A-site and the X-site elements to meet the desired value. We have also considered organic cation, MA<sup>+</sup> or FA<sup>+</sup>, to occupy the A-site in A<sub>2</sub>TiI<sub>6</sub> HPs, which are oriented in [001] and [100] directions, respectively. The results show that MA2TiI6 and FA2TiI6 HPs exhibit bandgaps of 1.67 and 1.70 eV, respectively. Other inorganic A<sub>2</sub>TiI<sub>6</sub> HPs, viz. K<sub>2</sub>TiI<sub>6</sub>, Rb<sub>2</sub>TiI<sub>6</sub>, Cs<sub>2</sub>TiI<sub>6</sub>, and In<sub>2</sub>TiI<sub>6</sub>, exhibit bandgaps of 1.55, 1.62, 1.65, and 1.40 eV, respectively. Although Rb<sub>2</sub>TiI<sub>6</sub> and Cs<sub>2</sub>TiI<sub>6</sub> possess slightly larger bandgap beyond the optimal region (0.9 to 1.6 eV), both HPs may still be suitable for certain PV applications.

The optical absorption is another important property that determines the suitability of a material for PV applications. Thus the absorption spectra of the HPs considered here are also computed, and they are compared with the absorption spectra of two popular PV materials, Si and MAPbI<sub>3</sub> HP, in Figure 1C. Compared with MAPbI<sub>3</sub>, all of the Pb-free HPs display relatively lower absorption intensity in the visible region but higher absorption in the lower-energy range. Overall, the HPs considered here still show good absorption behavior (with absorption coefficient >1.4  $\times$  10<sup>5</sup> cm<sup>-1</sup>). These favorable absorption properties render the Ti-based HPs promising candidates for PSCs. Figure 1D,E shows the computed band structures and density of state (DOS) of Cs2TiI6. Cs2TiI6 possesses an indirect fundamental bandgap between  $\Gamma$  (VBM) and X (CBM) and a direct bandgap at X, slightly larger than the indirect gap by  $\sim$ 30 meV. The band structure is similar to that of Cs<sub>2</sub>PdBr<sub>6</sub><sup>27</sup> which may be considered as a quasi-direct band gap. An analysis of the orbital character of Cs<sub>2</sub>TiI<sub>6</sub> reveals that the highest valence bands (VBs) are contributed mostly by the I 5p orbital, while the lowest conduction bands (CBs) are contributed by the Ti 3d orbital at  $\Gamma$  and X (Figure S1 in the

Supporting Information (SI)). Similar to MAPbI<sub>3</sub>, the A-site cation Cs does not contribute to the highest VB and lowest CB at  $\Gamma$  and X.

For Pb-containing HPs, spin-orbit coupling (SOC) can lower the computed bandgap significantly.<sup>29,30</sup> Here we show that the effect of SOC is quite small on the computed bandgap of  $Cs_2TiI_6$  (Figure S2): The computed bandgap is only narrowed slightly to 1.50 eV when SOC is considered. In fact, with SOC, the computed bandgaps are reduced slightly in all the Ti-based HPs considered here. This is expected because SOC becomes less important in materials containing light elements (Ti, Z = 22), as compared with those containing Pb (Z = 82). Interestingly, as the radius of A-site atom decreases, the bandgap decreases in the order  $In_2TiI_6 < K_2TiI_6 < Rb_2TiI_6$ < Cs<sub>2</sub>TiI<sub>6</sub>. The highest VB and lowest CB are contributed mainly by cation B and anion X. Hence, the A-site element does not seem to contribute directly to the electronic properties of HPs but can indirectly affect the electronic properties via altering the tilting of the  $[BX_6]^{2-}$  octahedra and the distance between adjacent octahedra.

To assess the structural stability of the HPs, we have calculated their decomposition energies with respect to several possible decomposition pathways.<sup>31</sup> Because MAPbI<sub>3</sub>, CsSnI<sub>3</sub>, and CsPbI3 HPs can be synthesized successfully using the corresponding binary halides (MAI, PbI<sub>2</sub>, CsI, SnI<sub>2</sub>, etc.), we can use the same approach to synthesize Ti-based HPs considered here. As expected, the predominant decomposition pathways are the reverse reactions of the corresponding synthesis routes. Also, there may be ternary products involved in other decomposition pathways. Thus, in this study, the decomposition enthalpy of different decomposition pathways is defined as  $\Delta H = 2E[AI] + E[BI_4] - E[A_2BI_6]$  or  $\Delta H = E[ABI_3] + E[AI_3] - E[A_2BI_6]$ . Here a positive value of  $\Delta H$  represents energy gain from the formation of decomposition products from the corresponding HPs. Figure S3 shows the calculated  $\Delta H$  values for the four HPs with different decomposition processes. It can be seen that all of the HPs considered here exhibit good stability with positive  $\Delta H$ values. Clearly, Cs2TiI6 and Rb2TiI6 HPs possess robust thermodynamic stability due to the fairly large positive values of  $\Delta H > 50 \text{ meV/atom}$ , suggesting the likelihood of experimental realization of these HPs. Moreover, ab initio molecular dynamic (AIMD) simulations were performed to examine the thermal stability of the four HPs. Figure S4 shows snapshots of the four HPs at initial time and 5 ps after the AIMD simulations. In the AIMD simulations, the temperature is maintained at 300 or 500 K. Note that the overall framework of the HPs is sustained in the final configuration at 300 or 500 K. When the temperature increases from 300 to 500 K, the  $[BX_6]^{2-}$  octahedra in the final configuration appear to have higher degrees of freedom, such as tilting. Hence the HPs considered here are likely to have good intrinsic stability up to very high temperatures, consistent with the analyses based on the decomposition energies.

Defect properties of the light absorbers in PVs are also important for their performance.<sup>32,33</sup> Here defect formation energies are calculated to assess the transport and optical properties of Cs<sub>2</sub>TiI<sub>6</sub> HP. We have considered a total of 12 possible intrinsic point defects in Cs<sub>2</sub>TiI<sub>6</sub> HP, including three types of vacancies ( $V_{\mu} V_{T\nu}$  and  $V_{Cs}$ ), three types of interstitials  $(I_{i_{r}} Ti_{i_{r}} and Cs_{i_{t}})$ , two cation substitutions  $(Ti_{Cs} and Cs_{Ti})$ , and four antisite substitutions (I<sub>Ti</sub>, I<sub>Cs</sub>, Ti<sub>L</sub>, and Cs<sub>I</sub>). Considering the thermodynamic equilibrium growth conditions, the formation energies of point defects are mostly dependent on the chemical potentials of the host elements,  $\mu_{I}$ ,  $\mu_{Ti}$ , and  $\mu_{Cs}$ . A moderate chemical potential region is identified for achieving thermodynamically stable Cs2TiI6. The identified chemicalpotential region for Cs<sub>2</sub>TiI<sub>6</sub> HP is highlighted in gray in Figure 2A. To calculate the formation energies, we focus on two extreme cases marked by two solid black circles in Figure 2: ( $\alpha$ ) I-rich/Ti-lean and  $(\beta)$  I-lean/Ti-rich. Under the I-rich and Tilean conditions, V<sub>I</sub> has the lowest formation energy, and it may act as a recombination center for a photogenerated electronhole pair (see Figure 2B). The acceptors  $I_{T\nu}$   $I_{\nu}$  and  $V_{Cs}$  also have relatively low formation energies. Because of the neutral charge state in the bandgap, they do not affect the electronic and PV properties significantly. It can be seen that the Fermi level induced by compensation of charged acceptor and donor defects is pinned slightly below the CB minimum (CBM), resulting in *n*-type conductivity, as is in the case of  $TiO_2$ . Under I-lean/Ti-rich conditions, the Cs<sub>i</sub> and Ti<sub>i</sub> have the lowest formation energy and are the dominant defects. However, because of the resulting deep defect states, both defects may be more detrimental to PV performance than the defects under Irich/Ti-lean conditions (see Figure 2C). The Fermi level is pinned above the CBM, indicating degenerate n-type conductivity in the Cs2TiI6 HP. These results suggest that under I-rich/Ti-lean growth conditions the deep-level defects can be suppressed in the synthesis of Cs<sub>2</sub>TiI<sub>6</sub> HP.

To support the theoretical predictions, a series of  $Cs_2TiI_xBr_{6-x}$  (x = 0, 2, 4, 6) HPs were chosen for experimental synthesis using the melt-crystallization method. First consider the end members,  $Cs_2TiI_6$  and  $Cs_2TiBr_6$  HPs. Figures 3A and Figure S5 show, respectively, the experimental and calculated X-ray diffraction (XRD) patterns of  $Cs_2TiI_6$  and  $Cs_2TiBr_6$ , confirming their phase purity. The Tauc plot of the  $Cs_2TiI_6$  and  $Cs_2TiBr_6$  HPs are ~1.02 and ~1.78 eV, respectively. The bandgap of  $Cs_2TiI_6$  is within the optimal bandgap range (0.9 to 1.6 eV) for single-junction PSCs.<sup>34</sup> Note that these are the first experimental bandgap (~1.51 eV) of MAPbI<sub>3</sub> was also measured



Figure 3. (A) Experimentally measured XRD patterns of  $Cs_2TiI_6$ ,  $Cs_2TiI_4Br_2$ ,  $Cs_2TiI_2Br_4$ , and  $Cs_2TiBr_6$  HPs (insets: photographs of the as-synthesized materials). (B) Expanded XRD patterns. (C) Experimentally measured absorption spectra of  $Cs_2TiI_6$ ,  $Cs_2TiI_4Br_2$ ,  $Cs_2TiI_2Br_4$ , and  $Cs_2TiBr_6$  HPs.

independently as a benchmark for this study (Figure S7). The measured bandgaps are slightly smaller than the computed HSE06 bandgaps. It is known that the hybrid functional HSE06 includes a fraction parameter  $\alpha$  (default value 0.25) for the screened short-range Hartree–Fock exchange to improve the derivative discontinuity of the Kohn–Sham potential for integer electron numbers. For certain compounds,  $\alpha$  parameter should be adjusted to yield a more accurate bandgap. Using TiO<sub>2</sub> as an example, when the value of  $\alpha$  is set at 0.20 or 0.21, the computed bandgap is in agreement with measured bandgap.<sup>35</sup> When  $\alpha$  value is set at 0.16, the computed bandgaps of Cs<sub>2</sub>TiI<sub>6</sub> and Cs<sub>2</sub>TiBr<sub>6</sub> HPs are ~1.05 and ~1.89 eV, respectively, which are in closer agreement with the measured bandgaps (Figure S8).

It is well known that the Shockley-Queisser limit<sup>36</sup> suggests a bandgap of  $\sim 1.3$  eV for achieving maximum PCE in a single p-n junction solar cell. To prepare the HPs with this ideal bandgap, one can tune the bandgap using doping or alloying strategies that have been studied extensively.<sup>37,38</sup> Because B<sup>4+</sup> and X<sup>-</sup> contribute to the CB and the VB, the bandgap can be tuned by replacing either B<sup>4+</sup> or X<sup>-</sup>. Intuitively, the replacement of X<sup>-</sup> can be achieved more easily experimentally. Thus mixed-I/Br HPs, Cs2TiI2Br4 and Cs2TiI4Br2, were synthesized and their properties were investigated experimentally and computationally. As shown in Figure 3A, the XRD patterns for Cs<sub>2</sub>TiI<sub>4</sub>Br<sub>2</sub> and Cs<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> and the end members, Cs<sub>2</sub>TiI<sub>6</sub> and Cs<sub>2</sub>TiBr<sub>6</sub>, exhibit similar features. This is expected because these HPs are isostructural solid-solutions. The 222 reflection shifts to higher  $2\theta$  with decreasing I/Br ratio (Figure 3B), as the gradual substitution of the larger I<sup>-</sup> with the smaller Br<sup>-</sup> shrinks the lattice parameter. The simulated XRD results for Cs<sub>2</sub>TiI<sub>6</sub> and Cs<sub>2</sub>TiBr<sub>6</sub> confirm the shift and are in good agreement with the experimental results (Figure S5). The lattice parameter, a, of Cs<sub>2</sub>TiI<sub>6</sub> Cs<sub>2</sub>TiI<sub>4</sub>Br<sub>2</sub>, Cs<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub>, and



Figure 4. (A) Schematic crystal structure of mixed-I/Br  $Cs_2TiI_xBr_{6-x}$  HPs. (B) Computed bandgaps of a series of  $Cs_2TiI_xBr_{6-x}$  HPs, using the HSE06 functional ( $\alpha = 0.16$ ) with and without SOC, and experimental data. (C) Computed optical absorption spectra (based on the HSE06 functional,  $\alpha = 0.16$ ) of  $Cs_2TiI_6$ ,  $Cs_2TiI_2Br_4$ ,  $Cs_2TiI_2Br_4$ , and  $Cs_2TiBr_6$  HPs compared with absorption spectra of Si and MAPbI<sub>3</sub> HP. (D) Computed band structure of  $Cs_2TiI_2Br_4$ , HP with space group I4/mmm (139) (Figure S9) using PBE functional; here  $\Gamma$  (0.0, 0.0, 0.0), Z (0.5, 0.5, -0.5), X (0.0, 0.0, 0.5), P (0.25, 0.25), and N (0.0, 0.5, 0.0) refer to the high-symmetry special points in the first Brillouin zone. (E) Computed DOS and projected DOS of  $Cs_2TiI_2Br_4$  HP using the HSE06 functional ( $\alpha = 0.16$ ) with SOC.

 $Cs_2TiBr_6$  is estimated at 11.67, 11.43, 11.25, and 10.92 Å, respectively, and all crystals possess  $Fm\overline{3}m$  space group. The insets in Figure 3a are photographs of the corresponding assynthesized  $Cs_2TiI_xBr_{6-x}$  HPs. It can be seen that the color of the HPs becomes lighter as the I/Br ratio decreases. The experimentally measured bandgaps of the corresponding materials decrease almost linearly (Figures 4b and S6). The absorption spectra of  $Cs_2TiI_6$ ,  $Cs_2TiI_4Br_2$ ,  $Cs_2TiI_2Br_4$ , and  $Cs_2TiBr_6$  HPs in Figure 3C show a significant shift to higher energy levels in the visible region, consistent with the bandgap trend.

Figure 4A depicts schematically the crystal structure of the mixed-I/Br  $Cs_2TiI_xBr_{6-x}$  HPs. The calculated bandgaps appear to be in reasonable agreement with the experimental results (see Figure 4B and Table S1). It is noteworthy that the bandgaps can be reduced to ~0.1 eV considering the SOC effect. When the I/Br ratio exceeds 0.5, the calculated bandgap values of the HPs no longer decrease linearly. This is due to the different arrangement orders of I and Br sites chosen in our models. By calculating bandgaps of  $Cs_2TiI_4Br_2$  with different arrangement orders, we find that there is a difference of ~0.25 eV in the bandgap values. Thus on the basis of the experimental measurements and calculations the  $Cs_2TiI_2Br_4$  HP is found to possess a direct bandgap of 1.38 eV, making it an optimal

candidate for the light-absorber layer in single-junction PSCs. The  $Cs_2TiBr_6$  HP can be an optimal wide-bandgap material (1.8 eV) for application in the tandem PVs in conjunction with the low-bandgap (1.1 to 1.2 eV) materials such as Si.<sup>2</sup> This bandgap tunability also enables the realization of specific value of bandgap for extending the absorption of sunlight compared with the current Pb-containing HP absorber layers. We have also considered other B-site metals. Several new transition metals, that is, Zr, Hf, V, Nb, Mo, or W, can replace the Ti. However, our calculations suggest that the bandgaps of some of these HPs may be too wide, while others may become metallic.

Figure 4C shows computed absorption spectra of a series of HPs compared with computed absorption spectra of Si and MAPbI<sub>3</sub> HP. With increasing I/Br ratio the absorption is continuously red-shifted, consistent with the trend of bandgap change. The experimental UV-vis absorbance spectra and Tauc plots (Figures 3C and S6) also confirm this result. Note that the maximum absorption coefficient in the visible-light range decreases, proportional to the decrease in I-content in the HPs. This indicates that I-based HPs tend to yield better absorption than Br-based HPs. We also computed the band structures of  $Cs_2Til_2Br_4$  with different arrangement of the I and Br sites (Figures 4D and S9). Here we considered only two structures with space groups I4/mmm and Imm2. The structure



Figure 5. Initial structures (left panels) and snapshots (right panels) of (A)  $Cs_2TiBr_6$  and (C)  $Cs_2TiI_2Br_4$  after 5 ps of AIMD simulations 500 K. Experimentally measured XRD patterns of (B)  $Cs_2TiBr_6$  and (D)  $Cs_2TiI_2Br_4$  HP samples before and after exposure to thermal and moisture stresses. For the thermal stability testing, the samples were annealed at 473 K for 1 h. For the moisture stability testing, the samples were stored at 298 K for 4 h under 70% RH.

with *I4/mmm* space group is slightly more stable than that with *Imm2* space group (~30 meV). Interestingly, the structure with *I4/mmm* space group possesses a direct bandgap. In contrast, the structure with *Imm2* space group shows a quasi-direct bandgap, which is found to be similar to that in  $Cs_2TiI_6$  HP (Figure S9). From the computed DOS of  $Cs_2TiI_2Br_4$  HP, it can be seen that the highest VBs are mostly contributed by the I 5p orbitals, while the lowest CBs are mostly contributed by the Ti 3d orbitals (Figure 4E).

In addition, we calculated the isotropic electron and hole effective masses of  $Cs_2TiI_6$  and  $Cs_2TiBr_6$  at the X and  $\Gamma$  points, respectively, using PBE functional (see Table S2). Similar to  $Cs_2PbBr_{6}$ , <sup>27</sup> for holes in the case of  $Cs_2TiI_{6}$ , there are light and heavy hole effective masses, -0.79(l) and -1.58(h) m<sub>e</sub> at  $\Gamma$ point, respectively. The electrons have effective mass of 1.58  $m_{\rm e}$ . Although the effective masses are larger than those of Pbbased HPs, both materials have reasonable carrier mobilities for PV application. On the basis of the crystal Hamilton population (COHP) analysis<sup>39</sup> of the Ti-X interaction in Cs<sub>2</sub>TiI<sub>6</sub> and Cs<sub>2</sub>TiBr<sub>6</sub> HPs, we found that the states at the highest occupied band are primarily nonbonding, similar to the Sn-I interaction in  $Cs_2SnI_6$  (Figure S10). For  $Cs_2TiI_2Br_4$ , there are two interactions, Ti-Br and Ti-I; both possess profiles similar to those Cs<sub>2</sub>TiI<sub>6</sub> and Cs<sub>2</sub>TiBr<sub>6</sub> HPs. Because of the effect of crossinteraction, the bonding of Ti-I and antibonding of Ti-Br in Cs<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> also contribute slightly to the highest occupied band. The average integrated COHP values for Ti-I and Ti-Br bond are -2.77 and -2.53 for Cs<sub>2</sub>TiI<sub>6</sub> and Cs<sub>2</sub>TiBr<sub>6</sub>, respectively, indicating that the Ti-I bond exhibits more covalent characteristic than the Ti-Br bond. The Born effective charges Z\* for the Ti (IV) in Cs<sub>2</sub>TiI<sub>6</sub> and Cs<sub>2</sub>TiBr<sub>6</sub> are 5.29 and 4.36, respectively, confirming the higher degree of covalency in the Ti-I bonds (Table S3). For Cs<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> HP, the value of the Born effective charges for the Ti4+ is between Cs2TiI6 and Cs<sub>2</sub>TiBr<sub>6</sub> due to the alloying of Ti-I and Ti-Br bonds. The increased covalency is in the order  $Cs_2TiBr_6 < Cs_2TiI_2Br_4 <$ 

 $Cs_2TiI_6$ , which likely prevents the formation of halide vacancies in these HPs. Additionally, the calculated high-frequency dielectric tensors  $\epsilon_{ij}^{\infty}$  have the same trend, that is, in the order  $Cs_2TiBr_6 < Cs_2TiI_2Br_4 < Cs_2TiI_6$  (see Table S3).

For the realistic deployment of a PV material, its intrinsic stability and tolerance to environmental (e.g., thermal, moisture) stresses are extremely important. In this context, the stability of the most representative Cs<sub>2</sub>TiBr<sub>6</sub> and Cs<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> HPs is assessed as case studies. AIMD simulations were first performed to evaluate the intrinsic stability of the Cs<sub>2</sub>TiBr<sub>6</sub> and Cs<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> HP crystal structures. As shown in Figure 5A,C, very small perturbation in the crystal structures of both HPs is observed after 5 ps AIMD simulation, confirming the intrinsic stability of these materials up to 500 K. Experimentally, pristine HP samples were annealed at high temperature (473 K) in a N<sub>2</sub> atmosphere to evaluate their thermal tolerance and were then exposed to room-temperature (298 K) humid environment (70% RH) to assess their moisture stability. The XRD patterns shown in Figure 5B,D indicate no degradation in both Cs<sub>2</sub>TiBr<sub>6</sub> and Cs2TiI2Br4 HP samples after the applications of the thermal/moisture stresses. For comparison, the widely studied MAPbI<sub>2</sub>Br and MAPbI<sub>3</sub> HPs with bandgaps close to those of Cs<sub>2</sub>TiBr<sub>6</sub> and Cs<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> HPs, respectively, show severe decomposition under the same conditions (Figure S11). These results clearly validate the superior stability of the Tibased HPs compared with the popular Pb-based HPs. The improved stability can be attributed to the all-inorganic nature and the highly stable covalent/ionic interaction between Ti (IV) and halide ions in the Ti-based HPs.

In summary, we have predicted a series of vacancy-ordered Ti-based, Pb-free HPs for PSCs application. We have found that  $Cs_2TiI_6$ ,  $Rb_2TiI_6$ ,  $K_2TiI_6$ , and  $In_2TiI_6$  HPs possess desired electronic and optical properties as visible-light absorber materials for PV applications. Despite the presence of ordered B-site vacancies, the band structures of this family of HPs show fairly dispersive conduction. Through an integrated theoretical

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and experimental effort, we have shown that the  $Cs_2TiI_2Br_4$  and  $Cs_2TiBr_6$  HPs possess bandgaps of ~1.38 and ~1.78 eV, ideally suitable for single-junction PSC and tandem PV application, respectively. It is also significant that both HP materials exhibit high intrinsic/environmental stability, superior to the popular Pb-containing HPs. Thus, this study shows that the new Tibased HPs can address both the Pb-contamination and the organic-cation volatility issues associated with the prevailing Pb-containing hybrid perovskites. It is envisioned that continued exploration of this promising family of HPs in the direction of solution/vapor processing and materials/device engineering is likely to lead to PSCs that can be efficient, nontoxic, intrinsically/environmentally stable, and cost-effective.

## COMPUTATIONAL METHODS

All first-principles computations were performed based on DFT methods as implemented in the Vienna ab initio simulation package (VASP 5.4).<sup>40</sup> An energy cutoff of 520 eV is employed, and the atomic positions are optimized using the conjugate gradient scheme without any symmetric restrictions until the maximum force on each atom is <0.02 eVÅ<sup>-1</sup>. The electronic structures and the optical properties are computed using the HSE06 functional<sup>41</sup> and with a cutoff energy of 400 eV, and the ion cores are described by using the projector augmented wave (PAW) method.<sup>42</sup> Grimme's DFT-D3 correction is adopted to describe the long-range van der Waals interaction.<sup>43</sup> A  $3 \times 3 \times$ 3 k-point grid is used for the Ti vacancy-ordered HPs. The optical absorption coefficient is given by  $\frac{\sqrt{2}\epsilon}{\hbar c} \left[ (\epsilon_1^2 + \epsilon_2^2) \frac{1}{2} - \epsilon_1 \right]^{1/2}$ , where  $\epsilon_1$  and  $\epsilon_2$  are real and imaginary parts of dielectric function, respectively. The initial configurations of A<sub>2</sub>TiI<sub>6</sub> with  $\sqrt{2} \times \sqrt{2} \times 2$  supercell (144 atoms) are adopted for AIMD simulations. Each 5 ps AIMD simulation is performed in the constant-volume and constanttemperature (NVT) ensemble. The time step is 1.0 fs, and the temperature (300 or 500 K) is controlled using the Nosé-Hoover method.44 More detailed computational description of the defects is included in the SI.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.7b01167.

Computational and experimental details. Additional calculations and characterization/analysis data in Figures S1–S11 and Tables S1–S3. (PDF)

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The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (NSF; OIA-1538893). M.G.J. and X.C.Z. received additional support from the University of Nebraska Holland Computing Center. X.C.Z. was also supported by the NSF MRSEC (DMR-1420645).

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