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Rational Design: A High-Throughput Computational Screening and Experimental Validation Methodology for Lead-Free and Emergent Hybrid Perovskites

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ABSTRACT: Perovskite solar cells, with efficiencies of 22.1%, are the only solution-processable technology to outperform multicrystalline silicon and thin-film solar cells. Whereas substantial progress has been made in scalability and stability, toxicity concerns drive the need for lead replacement, intensifying research into the broad palette of elemental substitutions, solid solutions, and multidimensional structures. Perovskites have gone from comprising three to more than eight (CH_3NH_3 , $\text{HC}(\text{NH}_2)_2$, Cs, Rb, Pb, Sn, I, Br) organic and inorganic constituents, and a variety of new embodiments including layered, double perovskites, and metal-deficient perovskites are being explored. Although most experimentation is guided by intuition and trial-and-error-based Edisonian approaches, rational strategies underpinned by computational screening and targeted experimental validation are emerging. In addressing emergent perovskites, this perspective discusses the rational design methodology leveraging density-functional-theory-based high-throughput computational screening coupled to downselection strategies to accelerate the discovery of materials and industrialization of perovskite solar cells.

The organic–inorganic hybrid perovskites^{1–3} have emerged in recent years as an exceptional class of materials delivering >22% solar cell conversion efficiencies, displaying promising light-emission properties, and exhibiting extraordinary phenomena relating to spintronics, photostriction, laser-cooling, and long-wavelength radiation detection, among others.^{4–6} These phenomena have been made possible by intrinsic properties of halide perovskites, exemplified by MAPbI_3 ($\text{MA} = \text{CH}_3\text{NH}_3$), that include defect-free, crystalline film formation at <100 °C, high optical absorption/emission with wavelength tunability, long-range ambipolar transport, efficient charge transfer, and injection to and from metallic contacts. These superior properties have been made possible by synergistic effects of the perovskite symmetry (monovalent cation, e.g., MA^+ , contained within a cuboctahedral cage comprising MX_6 metal halides) and lone-pair s orbitals that yield direct band gap p–p transitions.⁷

Despite the promising progress in high-efficiency solar cells,^{8–14} long-term stability and toxicity concerns due to the

presence of lead are two key issues that must be addressed before any market viability of perovskite solar cells could be suggested. Fortunately, perovskites offer a multitude of crystallographic configurations, along with a wide palette of substituents that portend the promise of new and exciting optoelectronic characteristics and enhanced device performance while resolving concerns of stability and toxicity.

Whereas stability issues are mainly being addressed through multication substitution, carbon encapsulation, and incorporation of hydrophobic moieties, the toxicity concern has taken a distinct route that relies on replacing Pb with divalent, trivalent, or tetravalent cations in perovskite and perovskite-related structures, including metal-deficient iodosalts, dimers, layered structures, and mixed and multidimensional perovskites. A typical

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process in identifying new variants relies on experience-driven short-listing and trial-and-error methodologies. However, the composition space is extremely large. Taking, for example, the nominal perovskite composition AMX_3 , although the choice of halide anions has been limited to Cl, Br, and I, the list of viable monovalent cations on the A site has been continuously expanding. Additionally, within the past few years high-efficiency materials have been realized with solid solutions of four cations on the A site: MA, FA (FA= formamidinium - $HC(NH_2)_2^+$), Cs, and Rb.^{11–14} Significantly more possibilities are also being examined to replace Pb with other divalent cations, including many transition metals.^{15,16}

Pb-free strategies include replacement of Pb with di-, tri-, and tetra-valent cations in perovskites, iodosalts, dimers, layered structures, and mixed and multi-dimensional perovskites.

To get an idea of the composition space for AMX_3 perovskite halides, full and partial substitutions with a mere 6 monovalent cations (A-site), 27 divalent metal cations (M-site), and 3 halides could yield a staggering number of $>10^4$ combinations. The possibility of metal-deficient, double perovskites, and multidimensional perovskites will further increase possible combinations to $>10^6$. Clearly it is impractical to attempt finding the best candidate materials purely from an experimental route. This perspective, focusing on perovskite materials design and selection, outlines a rational design methodology that combines combinatorial computational high-throughput screening (HTC) with experimental validation to down-select and highlight the candidates that have the highest propensity for the synthesis of lead-free perovskites as promising photovoltaic absorbers.

Although materials' discovery is often guided by trial-and-error-based Edisonian approaches, rational strategies comprising computational screening and experimental validation are emerging.

Organo-metallic halide perovskites may be categorized into the following typologies based on their structure and the valence of the metallic cation. **Type-I. Divalent-Metal-Based Perovskites:** AMX_3 (A = Cs/Rb/K; M = Sn/Ge; X = halogens) or layered perovskites $A_2A'_{n-1}M_nX_{3n+1}$ (A' = cations that do not fit in the MX_6 cavity); **Type-II. Trivalent-Metal-Based Perovskites:** $A_3M_2X_9$ (A = Rb/Cs/MA/FA; M = Sb/Bi); **Type-III. Tetravalent-Metal-Based Perovskites:** A_2MX_6 (M in +4 state);

and **Type-IV. Double Perovskites** $A_2MM'X_6$ (M in +1 and M' in +3 states) (A = Cs/Rb/K; M = Ag/In; M' = Bi/Sb). It should be noted that the listed substituents are examples only and many more substituents may be considered.

With comparable ionic radii, Sn was the first to be considered for Pb replacement; indeed, Sn perovskites have been previously reported to demonstrate promising electrical properties.¹⁷ Electronic and optical properties computed by density functional theory (DFT)-based first-principles electronic structure calculations^{18–20} of Sn-doped methylammonium lead halide, $CH_3NH_3Pb_{1-x}Sn_xI_3$ ($x = 0, 0.25, 0.5, 0.75, 1.0$), revealed that tin doping affects the composition and nature of the valence-band maximum (VBM) and narrows the optical band gap, allowing absorption of visible light up to 1100 nm. Tin 5p-induced electronic states are highly delocalized in nature and are likely to improve the mobility. Sn doping also changes the shape of VBM by producing extra energy states above the VBM and is responsible for lowering the effective mass of holes (delocalized energy states compared with Pb), thus improving the hole mobility that leads to an increase in exciton diffusion length, which is beneficial for charge separation. While Sn-based perovskites are yet to reach double-digit efficiencies, Sn–Pb with FA–MA combinations have yielded promising results.^{9,10} Another possibility, Ge^{2+} , is a candidate for Pb replacement, and $CsGeI_3$, $MAGeI_3$, and $FAGeI_3$, all yielding rhombohedral $R3m$ crystal structure, have been already successfully synthesized (Figure 1). However, the oxidative instability of Sn and Ge severely limits their utilization for photovoltaic applications.

Layered perovskites, for example, $A_2A'_{n-1}M_nX_{3n+1}$ ($n = 1$, pure 2D layered; $n = \infty$, 3D structure), are formed by the inclusion of cations (A, A') that do not fit in the MX_6 cuboctahedral cavity. Varying the size of the organic cations and altering the A:MX₆ ratios results in multidimensional perovskites ($n > 1$ but less than ∞ yielding a quasi-2D layered structure) with controlled inorganic layer stacking (Figure 1). These multidimensional perovskites allow for a great compositional flexibility, can be processed in single^{21–24} or multistep processes, and hold the promise of band gap tunability important for tandem cells, tunable exciton binding energies, and atmospheric stability. Although a number of layered perovskites have been synthesized, limited solar cell trials have been reported,^{25,26} with poor efficiencies and air stabilities posing a serious challenge in these systems.

Beyond the substitutions of Pb with other +2 metal cations, another possible structure in perovskites introduces 3+ metal cations such as Bi or Sb. These elements, which have similar electronic configuration as Pb^{2+} also exhibiting the presence of ns^2 electrons, are expected to equip perovskites with the same defect tolerant properties imparted by Pb. However, the +3 oxidation state constrains the ability to form a 3D corner-sharing perovskite structure with halides and chalcogenides, leading to the formation of $A_3M_2X_9$ compounds with a dimer structure (with fused biocuboctahedron) or a layered structure (with corner sharing octahedron). While $Cs_3Sb_2I_9$ only forms the dimer structure, the smaller Rb cation stabilizes the layered $Rb_3Sb_2I_9$ form.^{27,28}

The Bi^{3+} cation, containing 6s lone-pair electrons, is isoelectronic to divalent group-IV cations and polarizable similar to Pb^{2+} . Bismuth halide crystal arrangements are similar to those in the lead halide perovskites, where one can observe distortions, vacancies, and various modes of aggregation of the MX_6 octahedra. In addition, Bi^{3+} exhibits a stronger tendency to

Figure 1. (a) Evolution of multidimensional perovskites: 2D perovskites ($n = 1, 2$), 3D perovskites ($n = \infty$), and mixed-dimensional perovskites, with n = metal halide lattices. Adapted with permission from ref 21. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Size effect of A cation on trivalent-metal-based perovskites ($A_3M_2X_9$) (reprinted from ref 28). (c) Stacking crystal structure of $(CH_3NH_3)_2CuCl_xBr_{4-x}$ hybrid perovskites. Reprinted from ref 26. (d) Double perovskites ($A_2^+M^+M^{3+}X_6$). (e) Transformation from $CsSnI_3$ to Cs_2SnI_6 .

form lower dimensional metal halide units, as compared with Pb^{2+} . Bismuth perovskites (e.g., $Cs_3Bi_2I_9$, $MA_3Bi_2I_9$) have been reported,^{27,28} composed of fused bioctahedral $(Bi_2I_9)^{3-}$ clusters surrounded by Cs or MA cations. Solar cell performance from these materials has been disappointing (highest efficiencies $\sim 1\%$), and high background carrier densities contributing to bulk recombination are one potential factor being considered.²⁸ It has been found in band structure calculations that the band gaps of layered K- and Rb-based hybrid perovskites^{27,28} are direct, whereas they are indirect for $Cs_3Bi_2I_9$. Materials based

on Sb^{3+} cations are also being explored for solar-cell applications, and DFT calculations suggest^{27,28} that these materials are promising if solution processability could be facilitated.

For Sn and Ge, the highest oxidation state is tetravalent. In the 4^+ state, these materials form iodosalts compounds with halide anions, with the formula A_2MX_6 , with $A = Cs^+$, $CH_3NH_3^+$, $HC(NH_2)_2^+$, and so on; $M = Sn, Ge$; and $X = Cl, Br, I$. These compounds^{29–32} exhibit good air and moisture stability, and Cs_2SnI_6 displaying excellent conductivity has been used in dye-sensitized solar cells as a hole-transporting material (HTM).

The tetravalent metallic cations may be considered as forming 0D structures with packing of isolated $(MX_6)^{2-}$ octahedra. The structures formed by these cations can also be described as a double perovskite ($A_2M_2X_6$) compound, obtained by removing half of the octahedral M atoms, thus yielding a metal deficient perovskite that may also be referred to as a molecular salt with A^+ cations and $(MX_6)^{2-}$ anions. These materials are generally reported to exhibit dispersive electronic band structures; however, there continues to be uncertainty over carrier densities and type of charge carriers. Cs_2SnI_6 exhibits a direct band gap of 1.3 eV at the Γ point, and the VBM and conduction band minimum (CBM) are constituted by filled I-5p orbitals and empty I-6p/Sn-5s orbitals, respectively.

In Cs_2SnI_6 , the dispersion widths in the valence and conduction bands are 1 and 0.5 eV, respectively, and this dispersive nature associated with the molecular $[SnI_6]^{2-}$ salt compound is arguably related to the high conductivity in these materials. As an absorber material,²⁴ Cs_2SnI_6 has been deposited on ZnO nanorods, yielding low solar conversion efficiencies ($\sim 1\%$).

Double perovskites ($A_2^+M^+M^{3+}X_6$; instead of $A^+M^{2+}X_6$) open up the possibility of incorporating 3+ cations into the perovskite structure. These materials bear resemblances with the transition from $CuInS_2$ to Cu_2ZnSnS_4 materials. Elpasolites, Cs_2NaBiX_6 , have been studied since the 1970s,³³ and these large band gap semiconductors have found applications in scintillators for detection of X-rays, gamma-rays, and neutrons. Oxide double perovskites ($A_2MM'O_6$) have been thoroughly explored over the past few decades and have been shown to be an extremely versatile framework accommodating cations with oxidation states ranging from 1+ to 7+ in the M and M' sites.^{34–39}

A wide variety of halide double perovskite possibilities^{34–39} have been reported such as $Cs_2M^+M^{3+}X_6$, with $B^{3+} = Bi, Sb$; $M = Cu, Ag, Au$; and $X = Cl, Br, I$. Introducing Ag yielded $Cs_2AgBiBr_6$ with an indirect band gap of 1.95 eV, while $Cs_2AgBiBr_6$ and $Cs_2AgBiCl_6$, also with indirect band gaps of 2.19 and 2.77 eV, respectively, have also been reported. The incorporation of Bi^{3+} into the $Cs_2AgBiBr_6$ double perovskite leads to photoluminescence lifetimes of 660 ns, suggesting suitability for photovoltaic applications, whereas the indirect band gap of 1.95 eV makes this material suitable for tandem cells. The crystal structure of $Cs_2AgBiBr_6$ belongs to the cubic $Fm\bar{3}m$ space group and is composed of two types of octahedra alternating in a rock-salt face-centered cubic structure. Through electronic structure calculations, it has been found that the stable chemical potential region for pure $Cs_2AgBiBr_6$ is not so broad.^{34–39} The intrinsic p-type conductivity of this material has been reported to be mainly due to the Ag vacancies that are shallow in nature. The dominant defects under the Br-rich growth conditions are then Bi vacancies and AgBi antisites, which are basically deep acceptors. To suppress the formation

of the deep defects, the growth of $\text{Cs}_2\text{AgBiBr}_6$ under Br-poor/Bi-rich conditions is being explored. Trivalent metals like Cr or Fe have also been combined with alkali cations to form double perovskites, and the first solution-processable double perovskite, $(\text{CH}_3\text{NH}_3)_2\text{KBiCl}_6$, displaying electronic and mechanical characteristics similar to lead chloride double perovskite $\text{CH}_3\text{NH}_3\text{PbCl}_3$, has recently been reported.⁴⁰

Rational design may be referred to as the methodology to conceive materials (e.g., new compounds, stoichiometric combinations) with targeted attributes, aided by high-throughput computational screening (HTC), supplemented by experimental validation. In the context of perovskites, the process flow for rational design is outlined in Figure 2. Similar rational design

Figure 2. Rational design flowchart combining combinatorial computational screening with targeted experimental validation.

methodologies have previously been applied to drug discovery, battery materials, and catalysis, among others,⁴¹ and in recent years, HTC has been used to guide accelerated materials discovery and design across a broad range of applications related to energy storage, conversion, and beyond,^{42–51} including photovoltaic absorbers.^{15,16}

To appreciate the large compositional space available in this context and hence the attractiveness of using computational methods for screening, considering cationic valence states and volume ratios, possible perovskites combinations estimated are $> 24\,138$ for AMX_3 , $> 31\,290$ for $\text{A}_3\text{M}_2\text{X}_9$, $> 22\,350$ for A_2MX_6 , and $> 9 \times 10^6$ for $\text{A}_2\text{MM}'\text{X}_6$. For these estimations, 12 – A^{1+} (e.g., $\text{MA}^+/\text{FA}^+/\text{Cs}^+$), 27 – M^{2+} , 35 – M^{3+} , and 25 – M^{4+} site cations were chosen. In addition, three halogens (I^- , Br^- , Cl^-) and a maximum of three elemental substitutions per site (e.g., MA^+ , FA^+ , Cs^+ for the A-site) were considered. Clearly, we already have perovskites with at least four A-site cations, and thus these numbers may be considered as the lower bound of possible perovskite combinations.

The process outlined in Figure 2 may be outlined in the following steps:

Step I – Identify Target Structures: Begin with queries of possible structures from the Inorganic Crystal Structure Database (ICSD).

Step II – Energetics and energetic stability screening: Based on electronic structure calculations with computationally efficient

semilocal, for example, generalized-gradient-approximation, DFT methods.

Step III – Optical response screening: Filter based on screening through the essential descriptors of band gap (E_{gap}).

Step IV – Charge-carrier screening: Additional screening for carrier effective mass m^* and mobility of charge carriers.

Step V – Advanced electronic structure screening: Promising structures from initial screening to be subjected to more advanced electronic structure calculations such as hybrid exchange correlation functional and GW methods to derive accurate band structures and optical properties.

Step VI – Synthesis & Experimental Validation: The previous screening steps should be effective enough to enable down-selection to on the order of tens of materials that can be considered for experimental investigations. The experimental measurements would be correlated with the computational results, and, in some cases, this would lead to iterative computational screening—experimental validation steps to rationally discover compounds with the highest probability of high-performance photovoltaic characteristics. Following the identification of perovskite absorbers, the various interface layers also need to be identified, and a rational design approach toward this would be similarly more effective than an empirical trial-and-error approach.

With the four different typologies of perovskite systems described above and the large associated parameter space of possible compositions, the use of HTC as a tool for guiding the discovery of new compounds is highly attractive.^{42–51} For halide perovskites, while first-principles calculations have been applied extensively to understand structure–property relationships,^{52–54} HTC screening for the design and discovery of variants rivalling MAPbI_3 as photovoltaic absorbers has been less pursued.^{15,16,55–59}

HTC was used to screen AMX_3 inorganic halide perovskites¹⁵ with a goal of identifying Pb-free compounds with band gaps in the right range for photovoltaic applications. Results obtained in this study, considering a total of 360 different AMX_3 compositions (with $\text{A} = \text{K}$, Rb , Cs and $\text{X} = \text{Cl}$, Br , I and 40 different possible divalent M-site cations) in idealized cubic perovskite structures, are shown in Figure 3a. Because the results were based on semilocal exchange correlation potentials, the band gaps are significantly underestimated relative to experiment; nevertheless, the trends were found to hold up when the calculations were performed with alternative, more accurate functional. As described later in this Perspective, the calculations were further referenced with experimental studies.

Figure 3b shows the outcome of another computational screening study⁵⁵ for 116 possible metal halide perovskites with their corresponding band gaps. Another recent effort on computational screening used a method that combined HTC with random structure searches that focused on the electronic band gap and the perovskite crystal structure including compound stability.^{55–59} The authors reduced 248 potential perovskite combinations to 25, which were further down-selected to 15 for solar cell applications. Although this study was not coupled to experimental validation, the authors have identified Mg as a potential candidate for the partial replacement of Pb in organic–inorganic lead-halide perovskites.

In addition to identifying new materials, HTC can also be used to uncover materials design rules that are often elusive when only limited number of systems are studied. Castelli et al. calculated the band gaps of 250 perovskite halides AMX_3 and found that, in general, their band gaps⁵⁷ increase when A-site

Figure 3. (a) Predicted PBE functional band gaps of the 360 AMX_3 halide perovskite compositions. The top, middle, and bottom sections correspond to X-site species with halogens $X = \text{Cl}$, Br , and I , respectively, and in each session, the x and y axes correspond to M- and A-site components. Adapted with permission from ref 15. Copyright 2015 Royal Society of Chemistry. (b) Band gaps calculated for 116 possible metal halide perovskites. White represents band gaps larger than 3.5 eV, gray represents metallic structures, and all other colors represent band gaps between 0 and 3.5 eV. Adapted with permission from ref 55.

Figure 4. (a) Linear band gap variation with respect to the composition of Br in $\text{CsSnI}_{3-x}\text{Br}_x$ in coherence with Vegard's law. Reprinted from ref 61. (b) Calculated band gap tunability of the $\text{CsSnBr}_3\text{I}_{3-x}$. Theoretical predicted band gaps of CsSnBr_3 , CsSnBr_2I , CsSnBrI_2 , and CsSnI_3 with the Δ -sol method. The experimental results were also plotted here for comparing the trend of the band gap tuning. Adapted with permission from ref 42. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

cation changes from Cs to MA and further to FA; M-site cation from Sn to Pb; and X-site halide anion from I to Br and further to Cl. These trends follow those for the size of the ions well. Quite related to the finding of Castelli et al., Filip et al.⁵⁸ found that the band gaps of AMX_3 are strongly correlated with the largest metal–halide–metal bond angle, which can be controlled with the size of the molecular cations.

DFT-based deterministic HTC, while offering high fidelity, is still quite computationally expensive considering the large composition space and often the necessity of using “beyond-semilocal” methods for modeling excited-state properties and, in some systems, strong electron correlation. One way to address this problem is to pursue statistical machine learning. Using this approach, Pilania et al.⁵⁹ studied the formability of AMX_3 perovskite halides using a support vector machine classification model. Confirming the broadly used chemical intuition that steric packing determines the formability of perovskites, they found that ionic radii, tolerance factor, and

octahedral factor are the most important descriptors for their formability model. After validating and training this model, they were able to predict several novel AMX_3 perovskite halides with a high degree of confidence but at a significantly smaller computational cost than DFT.

A rational design methodology necessarily relies upon experimental synthesis and characterization of combinatorial HTC screening for calibration of the downselection process as well as validation of the potential materials in this case for photovoltaic applications. By calibrating the results (as outlined in Figure 4) against measured band gaps in the CsSnI_3 system, the authors¹⁵ identified CsGeI_3 , CsSnI_3 , CsSnBr_3 , and RbSnBr_3 as inorganic compounds^{60,61} with an appropriate band gap, which were also predicted to be thermodynamically stable. The calculations also predicted that replacing inorganic A-site cations by organic cations, to expand the lattice constant, would lead to increased band gaps; experimental results obtained for CsSnI_3 , CsGeI_3 , MAGeI_3 , and FAGeI_3 confirmed these predicted trends.

Table 1. Representative Device Performance of Lead-Free Perovskite Solar Cells

B cation	perovskite	E_{gap} (eV)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	ref
divalent	CsSnI ₃ (+ SnF ₂)	1.3	0.24	22.7	37	2.02	60
	MASnI ₃	1.23	0.88	16.8	42	6.4	23
	FASnI ₃ (+ SnF ₂ -Pyrazine)	1.41	0.29	24.5	55	4	20
	CsGeI ₃	1.63	0.074	5.7	27	0.11	15
	MAGeI ₃	2	0.15	4	30	0.2	15
trivalent	MA ₂ CuCl ₂ Br ₂	3	0.256	0.216	32	0.017	26
	Cs ₃ Bi ₂ I ₉	2.2	0.85	2.15	60	1.09	66
	MA ₃ Bi ₂ I ₉	2.1	0.68	0.52	33	0.12	66
	Rb ₃ Sb ₂ I ₉	2.24	0.55	2.11	56.97	0.66	28
	Cs ₃ Sb ₂ I ₉	2.05	0.31			<0.1	32
	MA ₃ Sb ₂ I ₉	2.14	0.89	1	55	0.5	67
	Cs ₂ SnI ₆	1.48	0.52	3.2	51.5	0.857	31

A subsequent thorough computational screening study by Korbel et al.,¹⁶ employing more accurate hybrid functional, leads to similar conclusions.

The band gap tunability in the case of CsSnBr_xI_{3-x} is an example⁴² where a comparison between theoretical prediction of band gap with a direct validation based on synthesis and characterization has been reported (Figure 4). CsSnI₃, CsSnBrI₂, CsSnBr₂I, and CsSnBr₃ are the four systems that were theoretically investigated, and the corresponding band gaps were determined using Δ -sol method.⁴³ Although the theoretical band gap values were uniformly larger than the corresponding experimental band gap values, a consistent trend of decreasing band gap with the decreasing concentration of iodine was observed. The results also confirmed that the wavelength tunability (in emission) was attributable to the partial halide substitution and not due to the mixing of different phases.⁴²

A materials screening strategy for oxide photovoltaics has been reported,⁶² and similar experimental screening efforts have been pursued for the discovery of solar fuels,⁶³ among others.

A major challenge for lead-free perovskites continues to be poor power conversion (Table 1), as none of the candidates have achieved double-digit efficiencies. Divalent Sn²⁺ and Ge²⁺ tend to oxidize into 4+ oxidation state, generating excessive defects (Sn and Ge vacancies), and result in short carrier diffusion lengths. However, a very recent study⁶⁴ reported single-crystal CsSnI₃ with smaller defect densities and significantly improved diffusion lengths, carrier life times, and a predicted efficiency of ~23%. Trivalent perovskites of Rb/Cs/MA with Sb and Bi have displayed very poor efficiencies, presumably due to high background carrier densities and high bulk recombination. The only report for tetravalent Sn⁴⁺, Cs₂SnI₆,³¹ yielded poor solar cell performance despite its direct band gap and Sn being in its stable 4+ oxidation state. The reason behind the poor performance is unclear, arguably a result⁶⁵ of its low electronic dimensionality, as the metal halide octahedra are either completely isolated in the dimer structure or disconnected along the stacking direction in the layered structure. Following this argument, it seems that mixing trivalent with monovalent cations in double perovskite structures is a promising direction. Nevertheless, we cannot find any report of device performance of double perovskite³⁴⁻⁴⁰ solar cells, despite many experimental and theoretical studies of the electronic and optoelectronic properties of metal halide double perovskites.

Beyond efficiencies, organo-halide perovskites continue their progress toward industrialization with scale-up efforts reporting certified efficiencies close to 10% for 70 cm² devices, > 96%

efficiency⁶⁸ retention upon 1 month of exposure to 95% relative humidity,⁶⁹ 1500 h of testing at 100 °C,⁷⁰ and stable performance upon exposure to up to 85 °C stress for 90 days.⁷¹ Addressing toxicity concerns, due to lead, is clearly the last major hurdle that needs to be cleared to establish viable industrialization potential. Lead-free material development is clearly in its divergent phase with efforts being focused on divalent, trivalent, and tetravalent metal cations and also with structures as diverse as layered, lower dimensionality materials, molecular salts, dimers, and double perovskites. Recent studies have indicated promising photovoltaic properties with Pb replacements such as Ni, Mg in the AMX₃; Sb, Bi in A₃M₂X₉; and Bi, Ag in the double perovskite families. These materials need further theoretical and experimental investigations to understand issues such as magnetic ordering, spin-orbit coupling, and trap defect states. Lead with its lone-pair s orbitals seems to play an indispensable role, and an approach for partial replacement of Pb with Sn and other transition metals appears to be gathering interest.^{9,10,55-59} Lessons learned from oxide perovskites, especially in the context of double perovskites, are encouraging, however, processability has proven to be a significant barrier, and new routes for solar cell fabrication are being explored.

It has also become evident that similar to superconductors, battery materials, and thermoelectrics, the pursuit of high-performance perovskites will lead to multiple dopants, substituents, and large degree of structural diversity. The quest for lead replacement will result in perovskite absorbers comprising multiple cations on both the A and M sites and also multihalide variants. These possibilities of structure and materials selection present us with >10⁶ perovskite combinations, necessitating a move away from empirical trial-and-error investigations toward a rational design methodology.

This perspective outlined the rational design paradigm, comprising high-throughput computational screening coupled to targeted experimental validation for lead-free perovskites. These theoretical and experimental screening strategies are still in their infancy; however, this method that has reaped rich dividends in the pharmaceutical industry promises us to offer similar breakthrough due to recent advances in first-principles calculations and significant progress in data sciences. Going forward, such rational design studies can be expanded to consider not only the band gap and thermodynamic stability but also additional bulk properties related to performance in a solar-cell device, such as dielectric constants, band alignments, and optical properties. Such calculations can also be extended to explore defect physics, which can be used to predict carrier

densities and transition levels under different experimental synthesis conditions. Such calculations are useful for identifying situations that lead to deep traps that can compromise photovoltaic performance. In recognition of the fact that the interface defines the device, the selection of perovskite absorber materials should then be complemented with an appropriate selection of interface materials, and in this selection, the rational design methodology would also be useful to guide device design. Overall, it can be expected that modern first-principles computational tools will continue to find broad use in fundamental studies of known perovskite solar cell materials as well as being used as a tool for accelerating the discovery of new materials in this context.

First-principles computational tools will advance fundamental studies of known perovskite materials and will be an essential tool for accelerating the discovery of new materials.

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