

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/325301159>

Toward Eco-friendly and Stable Perovskite Materials for Photovoltaics

Article · May 2018

DOI: 10.1016/j.joule.2018.04.026

CITATIONS

5

READS

410

7 authors, including:



Ming-Gang Ju

University of Nebraska at Lincoln

38 PUBLICATIONS 365 CITATIONS

[SEE PROFILE](#)



Min Chen

Brown University

16 PUBLICATIONS 173 CITATIONS

[SEE PROFILE](#)



Liang Ma

Southeast University (China)

34 PUBLICATIONS 516 CITATIONS

[SEE PROFILE](#)



Nitin Padture

Brown University

233 PUBLICATIONS 12,330 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Defect management in perovskite solar cells [View project](#)



2D hybrid perovskite [View project](#)

Perspective

Toward Eco-friendly and Stable Perovskite Materials for Photovoltaics

Ming-Gang Ju,^{1,4} Min Chen,^{2,4} Yuanyuan Zhou,^{2,*} Jun Dai,¹ Liang Ma,¹ Nitin P. Padture,^{2,*} and Xiao Cheng Zeng^{1,3,5,*}

The discovery and development of new Pb-free perovskite light-absorber materials that are eco-friendly and stable has become an active research area in the field of photovoltaics (PVs). These perovskites are being considered for possibly replacing the Pb-based organic-inorganic halide perovskites in state-of-the-art perovskite solar cells. While the recent effort in this area has led to certain progress, some scientific and technological issues still remain unresolved. Here we provide perspectives on the comprehensive understanding of perovskite toxicity/instability, followed by design strategies for new nontoxic, stable perovskites. We also envision unprecedented challenges in the processing of the promising candidate perovskites that bridges materials design and actual devices. Future research in these directions will open up new possibilities in realizing eco-friendly and stable perovskite PVs for real-world applications.

Introduction

Solar power is the most abundant, free, and sustainable energy source, but the cost of harvesting solar power using conventional photovoltaics (PVs) still remains high compared with the conventional fossil-fuel energy source in most places.^{1,2} Therefore, there is a pressing need to develop next-generation PVs that are not only highly efficient but also sufficiently inexpensive. In this context, a new thin-film PV technology, perovskite solar cells (PSCs), has emerged in recent years, which has received enormous attention and quickly rekindled research in the field of emerging PVs.^{3–5} Within a short period of time, the power conversion efficiency (PCE) of PSCs has experienced a rapid increase from 3.8% in the first-version PSC by Kojima et al.⁶ in 2009 to a certified 22.1% in 2017.⁷ At the heart of the PSCs are perovskite-type materials that are utilized as light absorbers. Since the early stages of PSC development, the most widely studied perovskites are Pb-based organic-inorganic halide perovskites (OIHPs), which have a general chemical formula of ABX_3 , where $A = CH_3NH_3^+$ (MA^+) or $HC(NH_2)_2^+$ (FA^+); $B = Pb^{2+}$; and $X = I^-$, Br^- , or Cl^- (see the left panel in Figure 1).^{8,9} Recently, the family of perovskite absorber materials has been expanded to embrace a wider variety of perovskite derivatives and variants such as “low-dimensional” (two-dimensional/one-dimensional/zero-dimensional) perovskites and chalcogenide perovskites.^{10–13}

While there is a surge of research activity in exploring alternative perovskite materials for PSCs, the state-of-the-art PSCs still require Pb^{2+} as the B-site cation in the perovskite crystal structure. Assuming that all of the US electricity need is generated using PSCs based on the most widely studied Pb-based OIHP, $MAPbI_3$ (38 μg of Pb per 1 kWh), the annual use of Pb is estimated at 160 tons.¹⁴ Although effective regulation and management of the PSC life cycle can reduce the release of element Pb into the environment, it is obvious that the ultimate solution to the Pb-toxicity issue

Context & Scale

Solar power is the most abundant and free source of renewable and sustainable energy on Earth. In response to the pressing need to develop efficient, low-cost photovoltaics (PVs) to harness the solar power, perovskite solar cells (PSCs) have recently emerged as a potential disruptive PV technology. However, the state-of-the-art PSCs employ lead-based organic-inorganic halide perovskites as light absorbers, raising concerns regarding their chemical stability and the use of toxic element lead (Pb) that may be released into the environment. Therefore, it is of long-term practical importance to develop eco-friendly, stable, and efficient perovskite materials for future PSCs that can eventually be commercialized. Moreover, discovery and development of these new perovskite materials will have profound implications on a broad range of (opto)electronic applications, including, but not limited to, solar cells, light-emitting devices, lasers, photodetectors, and X-ray imaging.

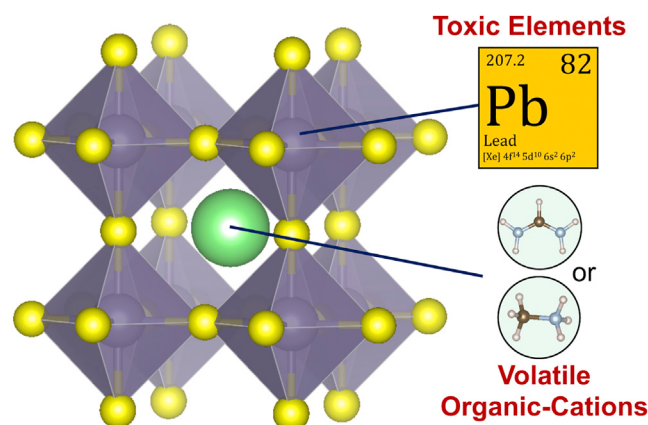


Figure 1. Schematic Illustration Showing the Crystal Structure of the Prevailing Pb-Based OIHPs

There is environmental concern due to the presence of the toxic element Pb, and the stability issue due to the presence of the organic cation (MA^+ or FA^+) at the A sites.

will be the elimination of Pb in PSCs. In particular, for niche consumer or household applications such as portable PVs, the allowable amount of toxic elements that can be included in such devices is extremely low.¹⁵ For example, the US OSHA (Occupational Safety and Health Administration) lists element Pb and its compounds as highly hazardous, and has set the legal permissible exposure limit in general industry to <0.05 mg/L.¹⁶ In addition, since the main health effects caused by Pb are narcosis and irritation of the eye/nose/throat, significant resources must be spent in protecting employee health against Pb exposure, which will inevitably increase the manufacturing cost of Pb-based PSCs. The other significant issue with the prevailing Pb-based bulk OIHPs is that they require organic cations such as MA^+ and FA^+ occupying the A-site in the perovskite structure. These organic species are relatively weakly bound to the metal-halide octahedra, which can be highly volatile under PSC operating conditions with respect to inorganic cations.¹⁷ The organic species are also highly hygroscopic as they contain $-\text{NH}_3$ functional groups in the crystal structure, which are prone to be attacked by H_2O and may accelerate the degradation of perovskites upon exposure to the open air.^{18,19} Thus, both issues, toxic element Pb and chemical instability, are major hurdles that will hold back the large-scale commercial deployment of PSCs based on Pb-containing bulk OIHPs. In order to tackle both issues, it is essential to develop new perovskite candidates that are nontoxic and stable, yet with reasonable PCE, for replacing the prevailing Pb-based OIHPs in PSCs. In this perspective, we first highlight the sense of urgency in understanding the origins of the toxicity and instability in the prevailing perovskite light-absorber materials, followed by a discussion of design strategies of new eco-friendly, stable perovskites. Lastly, we provide an outlook on the synthesis of new candidate Pb-free perovskite materials.

The Environmental Impacts and Stability of Promising New Perovskites Need to Be Assessed

As shown in Figure 2A, the typical life cycle of a PSC panel would follow the following steps: raw materials extraction, synthesis/processing, cell assembly, usage, and cell decommissioning.^{20,21} Although detailed life cycle assessment of the PSC technology is still premature at this stage, it is certain that the release of toxic species derived from perovskites will occur during all the above steps. This will invariably have a negative impact on the environment, such as land/water pollution, and

¹Department of Chemistry, University of Nebraska—Lincoln, Lincoln, NE 68588, USA

²School of Engineering, Brown University, Providence, RI 02912, USA

³Department of Chemical & Biomolecular Engineering and Department of Mechanical & Materials Engineering, University of Nebraska—Lincoln, Lincoln, NE 68588, USA

⁴These authors contributed equally

⁵Lead Contact

*Correspondence:
yuanyuan_zhou@brown.edu (Y.Z.),
nitin_padtare@brown.edu (N.P.P.),
xzeng1@unl.edu (X.C.Z.)

<https://doi.org/10.1016/j.joule.2018.04.026>

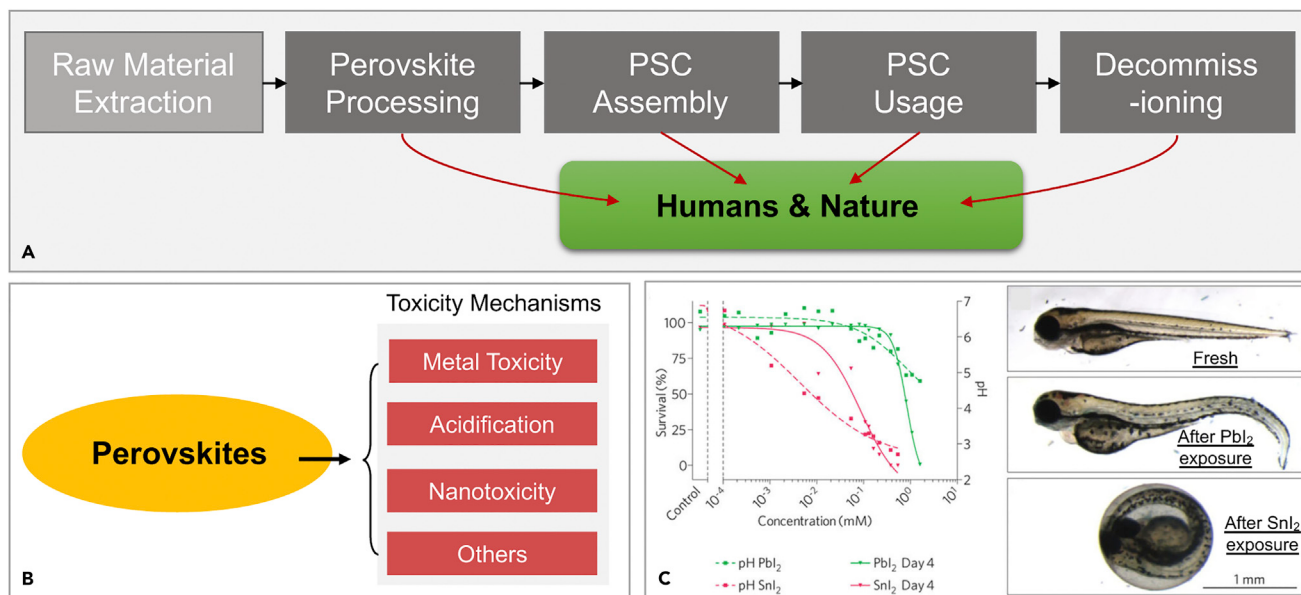


Figure 2. Assessment and Mechanisms of Toxicity in Perovskites

(A) The typical expected life cycle of perovskite solar panels. Re-drawn from Ref.²⁰.

(B) Potential toxicity mechanisms of perovskites.

(C) Results from biological experiments that have been used to assess the potential toxicity of Pb- and Sn-based perovskites. The plots show the survival of zebrafish after 4 days post-fertilization as a function of toxicant concentration and pH. The optical images show healthy zebrafish (top); zebrafish exposed to Pbl₂ (1.08×10^{-2} mM) showing a brain hemovascular defect, heart edema, and dorsal curvature (middle); and zebrafish embryo exposed to SnI₂ (1.62×10^{-1} mM) showing failed hatching 96 hr post-fertilization (bottom). Adapted from Ref.²⁰ with permission, Nature Publishing Group.

eventually the contaminants will end up in the food chain affecting human beings.²²

There is also concern of environmental impacts resulting from potential catastrophic events such as fire or flooding involving PSC manufacturing, transportation, storage, and usage.²³ Thus, the environmental and health impacts are not just limited to the direct Pb metal toxicity. Furthermore, there can be several other mechanisms such as acidification and nanotoxicity that can make perovskites potentially harmful to the environment and human health (see Figure 2B). For example, Sn-based PSCs have achieved ~10% PCEs, and they are recognized as potential eco-friendly candidates for PSCs. However, Babayigit et al.²⁰ have recently found that the oxidation of Sn(II) to Sn(IV) in Sn-based perovskite materials can occur rapidly in ambient or aqueous environments, which leads to the formation of hydroiodic acid as a by-product.^{20,24} Results from biological experiments using zebrafish as a model (Figure 2C) indicate that SnI₂ exposure is more acutely toxic to zebrafish than Pbl₂ exposure, which seems counterintuitive. This is mainly due to the more severe acidification effects brought about by Sn²⁺ compared with Pb²⁺. Furthermore, both Pb-based and Pb-free perovskites are expected to be in nanoscale-size in PSCs and optoelectronic applications.^{25,26} Since nanoscale materials are known to be harmful to living cells and biological systems in some cases, nanoscale perovskite materials could be also potentially toxic. In addition to physicochemical properties, the production of possible fibrous structure,^{27,28} high surface charge state,^{25,29,30} and generation of radical species in nanoscale perovskites due to their size may prove to be harmful.³¹ Therefore, to have a reliable assessment of the toxicity of perovskite materials, both established and newly discovered ones, there is an urgent need to design and conduct a standard system of biological experiments toward this goal. Research in this direction is still rare, and it may emerge as an important area in the field of PSCs.

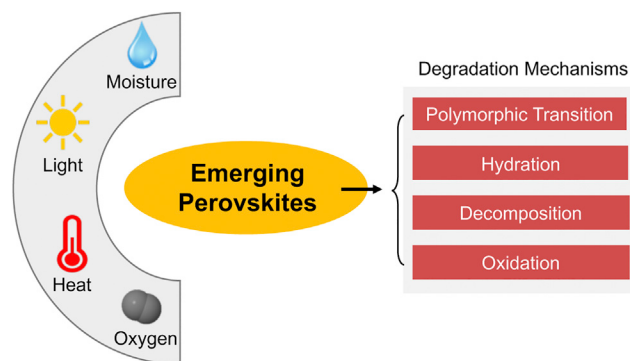


Figure 3. Schematic Illustration of the Environmental Factors and Mechanisms that Are Responsible for the Degradation of Emerging Perovskite Materials

Regarding stability, as shown in Figure 3, the most significant factors that degrade a perovskite material include moisture, light, heat, and oxygen. These factors degrade OIHPs via a variety of mechanisms that include, but are not limited to, polymorphic transformation, hydration, ion diffusion,³² decomposition, and oxidation. In recent years, while the degradation in the prevailing Pb-based OIHPs has been studied comprehensively, understanding of the degradation of the emerging Pb-free perovskites is relatively scant. In fact, some results in the literature have indicated that the stability issue of the emerging perovskite materials can be even more complex than the Pb-based OIHPs. Several degradation mechanisms may be in play at the same time. For example, CsSnI₃ is a promising Pb-free candidate perovskite material with an optical bandgap of 1.3 eV and relatively high carrier mobility, which has attracted considerable interest.³³ Owing to its all-inorganic nature and strong covalent/ionic bonding in the crystal structure,³⁴ CsSnI₃ perovskite exhibits high thermal stability.³⁵ However, γ -CsSnI₃ “black” phase transform readily to δ -CsSnI₃ “yellow” polymorph upon exposure to the ambient environment.^{36,37} Meanwhile, Sn(II) in CsSnI₃ can be extremely susceptible to oxidation to Sn(IV) in the presence of oxygen, converting CsSnI₃ to Cs₂SnI₆.³⁸ In addition, it is also possible that the moisture in the ambient environment ingresses into CsSnI₃ perovskite thin films, forming hydrates and eventually decomposing CsSnI₃ to metal halides. These degradation mechanisms may occur simultaneously, causing rapid decrease in the PCE of CsSnI₃-based PSCs. In the case of high-PCE PSCs based on Sn-containing OIHPs (MASnI₃ or FASnI₃), their instability in ambient environment can be so severe that these PSCs degrade within several minutes if not encapsulated. To study these mechanisms separately is rather challenging, but there is a dire need for addressing the instability issue of PSCs fully. Furthermore, the stability and degradation of many other Pb-free perovskite candidates, such as CsGeI₃, CsSn_xGe_{1-x}I₃, Cs₂TiI_{6-x}Br_x, and Cs₂AgBiBrI₆, have been rarely studied.^{39–41} Their tolerance to the key environmental factors (moisture, light, heat, oxygen) and potential degradation pathways have not been revealed clearly, which will be a rich area of research. The exploration of the stability of these emerging perovskites will lead to fundamental scientific findings that will guide the design of new Pb-free, stable perovskites for PSCs.

There Is Urgent Need to Search for Nontoxic, Stable Perovskites for PVs through Integration of Theory and Experiment

Considering the large number of compounds in the perovskite family and its derivatives, it is necessary to adopt theoretical calculations as screening tools to identify potential candidate perovskites that are both nontoxic and stable. Such materials

screening procedures naturally involve two steps, as follows. The first step is to address the toxicity issue by finding candidate elements that could replace Pb in the prevailing Pb-based OIHPs. The replacements have to retain the main intrinsic electronic, transport, and optical properties (bandgap, carrier mobility, optical absorption, etc.) of perovskites for PV applications. In the literature, Sn^{2+} and Ge^{2+} , which are both in group IV of the periodic table, are natural alternatives for replacing Pb^{2+} . This thinking has driven the emergence of a group of Pb-free Sn- and Ge-based perovskites that show some promise for PV applications. In particular, although Sn^{2+} can be easily oxidized to Sn^{4+} , resulting in performance reduction, Sn-based PSCs have recently shown PCE close to 10%.⁴² An alternate way for identifying potential Pb-free perovskite candidates is from the view of electronic structure. In Pb-based OIHPs, the strong antibonding coupling of the Pb lone-pair 6s orbital with I 5p orbital leads to high-level band dispersion, ambipolar conductivity, and defect tolerance, which are responsible for long carrier lifetimes and diffusion lengths, resulting in high PCEs in PSCs made using these materials.⁴³ Therefore, much effort has been devoted to perovskites based on alternative metals such as In^{1+} , Ga^{1+} , Bi^{3+} , and Sb^{3+} that also contain lone-pair ns^2 .^{44–46} Also, the search can be conducted for new compounds containing antibonding coupling between different orbitals at valence band maximum, which may lead to a band-edge character similar to that in Pb-based perovskites. For example, Yin et al.⁴³ have suggested skutterudite-structure IrSb_3 has a p - p^* antibonding coupling band-edge character with respect to Pb-based perovskites. Another way to search the potential Pb-free perovskite candidates is from the view of crystal structure for perovskite materials. It is interesting that, for maintaining charge neutrality, replacing Pb^{2+} with an aliovalent metal cation will invariably result in perovskite structures with new chemical formulae $\text{A}_2\text{B(IV)X}_6$, $\text{A}_3\text{B(III)}_2\text{X}_9$, AB'(I)B''(III)X_6 , and AB(V)X_6 , which deviate from the standard AB(II)X_3 formula.^{40,47} This structural change will also affect the electronic structure of the compounds.⁴⁸ As shown in Figure 4A, by taking both the crystal structure and chemical composition into account, newly proposed perovskite-type compounds that exhibit favorable electronic structures for PV applications can be identified.

Stability of perovskites is a more complex problem, which is difficult to predict through a purely computational approach, and thus a theory-experiment integrated approach is necessary.^{49,50} Usually, Goldschmidt's tolerance factor (t) is a widely used empirical rule to roughly estimate perovskite phase stability. The range of $0.9 \leq t \leq 1$ is generally viewed as very good fit for perovskites, implying the likelihood of cubic structures, while the range of $0.71 \leq t \leq 0.9$ generally implies the likely formation of orthorhombic or rhombohedral structures due to the tilting of the octahedra. For $t \leq 0.71$ or $t \geq 1$, other structures, such as hexagonal or NH_4CdCl_3 -type, can form. Figure 4B shows a proposed flowchart for screening nontoxic-metal-based perovskite candidates with favorable stability for PVs using a rationally combined theory-experiment approach. This flowchart starts with a potentially promising nontoxic-metal-based Pb-free perovskite candidate identified using the methodology in Figure 4A. Since there is a fundamental stability issue with the intrinsically volatile organic A-site cations (MA^+ and FA^+), inorganic cations such as cesium (Cs^+),^{51,52} which exhibit much stronger covalent/ionic bonding with X-site anions, are used as replacements.^{19,53} By combining this A-site and B-site ion substitution, the promising perovskite candidates can be screened. While compounds such as CsSnI_3 , $\text{Cs}_2\text{AgBiBr}_6$, and Cs_2TiBr_6 have been successfully predicted and synthesized using this approach,^{35,40,46} other perovskite candidates that are potentially less toxic and more stable can be found. For example, stable divalent metals, such as Ca^{2+} , Mg^{2+} , Si^{2+} , and Zn^{2+} ,^{54,55}; many monovalent metals, such as Ag^+ , Au^+ , Cu^+ ,

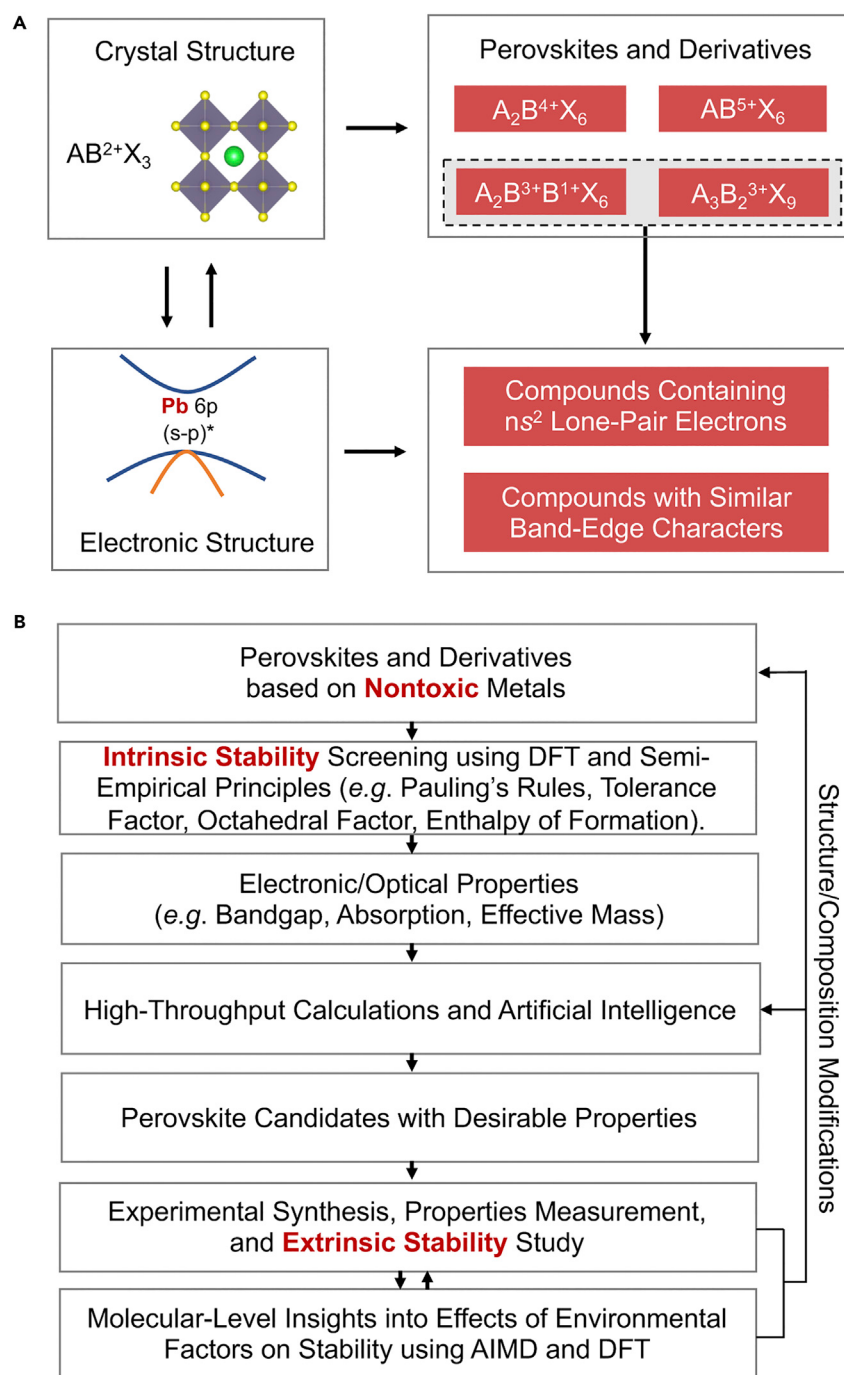


Figure 4. Methods for Searching for Nontoxic, Stable Perovskites

(A) Illustration of methodology for theoretically identifying nontoxic, stable perovskite candidates for PSCs from combined views of crystal structure and electronic structure.

(B) A flowchart to illustrate a process for searching ideal nontoxic, stable perovskite candidates for PSCs, including the use of a rationally integrated theory-experiment approach. AIMD, *ab initio* molecular dynamics; DFT, density functional theory.

and In^+ ; and trivalent metals, such as In^{3+} , Sb^{3+} , and $\text{Bi}^{3+56-58}$ have been suggested to replace B-site ions to form perovskite structures. In addition, it has been shown by Ju et al.⁴⁰ and Sakai et al.⁵⁹ that it is possible to replace the B-site ion with

tetravalence metal (B^{4+}), forming more stable vacancy-order double perovskites such as $Cs_2Ti(IV)Br_6$ and $Cs_2Pd(IV)Br_6$, respectively. Besides, the B-site ion can be replaced by the same atoms with different valence states (e.g., Au^+ and Au^{3+})⁶⁰ for electronic double perovskites.

In the general process flow shown in Figure 4B, the intrinsic or thermodynamic stabilities of new compounds are first confirmed using density functional theory (DFT)-based first-principles calculations (e.g., formation energy prediction), followed by examination of the critical PV-related electronic/optical properties. The perovskites are then synthesized and their stability/degradation under extrinsic environmental stresses (e.g., temperature, light, water, oxygen) are studied experimentally based on the methodology shown in Figure 3. The experimental study is also complemented by mechanistic studies using theoretical tools such as the Born-Oppenheimer molecular dynamics (MD) simulation and DFT-based methods (e.g., nudged elastic band). The results from these complementary theory-experiment studies provide directions in modifying the perovskite crystal structure/composition (ion replacements and doping/alloying)^{9,61} and finding potentially more stable perovskite candidates. Note that the key electronic structure and PV-related properties of the perovskites are carefully considered during the whole stability-screening process, as reflected in Figure 4B.

Moreover, combining computational quantum-mechanical, thermodynamic approaches and techniques rooted in database construction and intelligent data-mining, high-throughput computational materials design can be employed to predict Pb-free perovskite materials for PV applications. However, these calculations are still nowhere near direct simulation of materials, and they usually address only a small part of the actual design problem. More importantly, to describe key properties (e.g., stability, light absorption, carrier mobility, low cost, and nontoxicity) for material function, the descriptors can be computed at the DFT level for screening candidate materials. As mentioned earlier, the computational descriptors of intrinsic stability are Pauling's rules, tolerance factor, octahedral factor, atomic packing fractions,⁶² and enthalpy of formation. The descriptor of light absorption and carrier mobility may be approximately related to the bandgaps and effective masses of materials. Low cost and nontoxicity of materials can, at least to some extent, be estimated based on the constituent elements. On the basis of aforementioned descriptors, one can screen the candidates with perovskite structure, and its derivatives, to search for suitable materials with desirable properties.^{55,63,64} However, considering the large composition space and the numerous suitable descriptors for key properties, which are usually obtained through more accurate functional, the high-throughput computational design is quite computationally expensive. In contrast, on the basis of known data, which already exist or are obtained by calculations, a proper machine learning model may be trained. This model can then be used to explore the periodic table in a search for new candidate materials with desirable properties, providing insights and guidance for experimentation. By finding important descriptors (e.g., Pauling's rules, tolerance factor, octahedral factor, electronegativity, average ionic radius, and number of valence electrons), the stability and bandgap of perovskites have been predicted using these approaches in previous reports.^{65–68}

The Emerging Pb-free Perovskites Need to Be Processed into Thin Films for Adaption into PSCs

Processability is another key factor for evaluating the promise of a new perovskite material for use in PVs. Thus, once candidate perovskites with good optical/electronic properties, nontoxicity, and favorable stability are identified, their thin-film

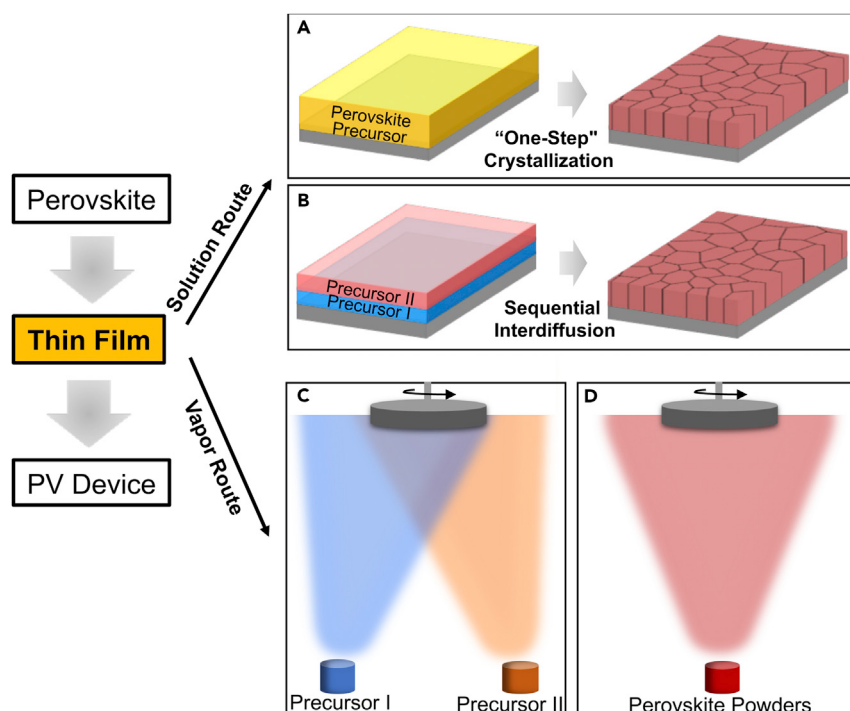


Figure 5. Methods for Processing of Nontoxic, Stable Perovskite Thin Films

(A–D) Schematic illustration showing thin film processing as a bridge between perovskite materials and PV devices, and the possible solution/vapor routes for the deposition of the new Pb-free perovskite thin films. (A) Direct solution growth from the perovskite precursors; (B) sequential growth based on inter-diffusion reactions of the as-deposited precursor phases; (C) dual-source co-evaporation of the precursors; (D) single-source evaporation of the perovskite.

processing needs to be explored in order to bridge the perovskite crystal design to thin-film-based PV devices, as shown in Figure 5. Solution-based processing is the most attractive for the development of PSCs, which can be broadly classified into two types: (1) “one-step” direct crystallization (Figure 5A) from solutions where the perovskite precursors are co-dissolved or the perovskite materials themselves can be dissolved,^{4,69} and (2) “two-step” sequential growth (Figure 5B) based on inter-diffusion reactions between stacked layers of precursor.^{70,71} Both methods have been widely and successfully employed for the synthesis of Pb-based OIHP thin films. However, for the new stable, nontoxic perovskite thin films, these two methods may not be applicable in a straightforward manner. Several challenges are envisioned. For the one-step method, it will be necessary to develop eco-friendly solvent systems that can easily co-dissolve the precursors, as the cations that replace Pb^{2+} in the perovskites may not exhibit high coordinative interaction with solvent molecules that help dissolution. For the two-step method, considering the possibility of more sluggish ion mobility, it could be challenging to accelerate the reaction kinetics for facilitating the formation of high-purity Pb-free perovskites. Also, solution deposition of the stacked layers using orthogonal solvents could be a potentially intractable issue due to limited solvent choices.

The vapor-based methods are typically divided into two categories: (1) co-evaporation of the precursors (Figure 5C); and (2) single-source evaporation of the as-synthesized perovskite powders (Figure 5D).^{3,72,73} While the vapor approach may appear straightforward compared with the solution approach, the relatively complex

compositions of new perovskites may render vapor-based methods rather difficult. Nevertheless, by performing detailed fundamental studies, many unknown physical/chemical characteristics of new perovskites can be understood. The knowledge gleaned from these studies will help the development of efficient strategies to resolve potential processing issues. Such experimentation may emerge as an attractive research topic in the roadmap for realizing nontoxic, stable PSCs.

Summary

The commercialization of PSCs calls for extensive research and development (R&D) efforts on new perovskite materials that are not only highly efficient in light-to-electricity conversion but also nontoxic and stable. Over the next few years, much increased R&D effort is expected to be devoted to the search for such new perovskite materials. While the current ongoing research activities toward this goal appear to progress in somewhat random directions, we suggest here a rational roadmap that may contribute to accelerating the R&D in this area. This roadmap starts with understanding the toxicity/degradation mechanisms of the current and emerging perovskites through more standardized experimental protocols. This is followed by the design (including complementary theory-experiment approaches) of new eco-friendly perovskites that can be highly resistant to environmental stresses, after gaining in-depth understanding of the toxicity/degradation mechanisms. We envision enormous challenges that still lie ahead regarding the experimental thin-film fabrication of the emerging lead-free, stable perovskites. The latter is a pivotal step toward successful and eventual device fabrication and manufacturing. At the same time, it also presents exciting opportunities for synthesis/processing innovations. By conducting combined scientific and engineering R&D along these lines, we expect that the realization of efficient and eco-friendly PSCs will take place in the future.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation (NSF; No. OIA-1538893). M.-G.J., J.D., L.M., and X.C.Z. acknowledge additional NSF support (no. DMR-1420645) and the UNL Holland Computing Center for this work.

REFERENCES

- Gratzel, M. (2014). The light and shade of perovskite solar cells. *Nat. Mater.* 13, 838–842.
- Green, M.A., Ho-Baillie, A., and Snaith, H.J. (2014). The emergence of perovskite solar cells. *Nat. Photon.* 8, 506.
- Liu, M., Johnston, M.B., and Snaith, H.J. (2013). Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* 501, 395.
- Jeon, N.J., Noh, J.H., Kim, Y.C., Yang, W.S., Ryu, S., and Seok, S.I. (2014). Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells. *Nat. Mater.* 13, 897.
- Correa-Baena, J.P., Saliba, M., Buonassisi, T., Gratzel, M., Abate, A., Tress, W., and Hagfeldt, A. (2017). Promises and challenges of perovskite solar cells. *Science* 358, 739–744.
- Kojima, A., Teshima, K., Shirai, Y., and Miyasaka, T. (2009). Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.* 131, 6050–6051.
- National Center for Photovoltaics, Best Research-Cell Efficiencies, National Renewable Energy Laboratory, <https://www.nrel.gov/pv/assets/images/efficiency-chart.png>.
- Kim, H.S., Lee, C.R., Im, J.H., Lee, K.B., Moehl, T., Marchioro, A., Moon, S.J., Humphry-Baker, R., Yum, J.H., Moser, J.E., et al. (2012). Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Sci. Rep.* 2, 591.
- Zhou, Y., Zhou, Z., Chen, M., Zong, Y., Huang, J., Pang, S., and Padture, N.P. (2016). Doping and alloying for improved perovskite solar cells. *J. Mater. Chem. A* 4, 17623–17635.
- Tsai, H., Nie, W., Blancon, J.C., Stoumpos, C.C., Asadpour, R., Harutyunyan, B., Neukirch, A.J., Verduzco, R., Crochet, J.J., Tretiak, S., et al. (2016). High-efficiency two-dimensional Ruddlesden–Popper perovskite solar cells. *Nature* 536, 312.
- Cao, D.H., Stoumpos, C.C., Farha, O.K., Hupp, J.T., and Kanatzidis, M.G. (2015). 2D homologous perovskites as light-absorbing materials for solar cell applications. *J. Am. Chem. Soc.* 137, 7843–7850.
- Snaith, H.J. (2013). Perovskites: the emergence of a new era for low-cost, high-efficiency solar cells. *J. Phys. Chem. Lett.* 4, 3623–3630.
- Xiao, Z., Zhou, Y., Hosono, H., Kamiya, T., and Padture, N.P. (2018). Bandgap optimization of perovskite semiconductors for photovoltaic applications. *Chemistry* 24, 2305–2316.
- Fabini, D. (2015). Quantifying the potential for lead pollution from halide perovskite photovoltaics. *J. Phys. Chem. Lett.* 6, 3546–3548.
- Hailegnaw, B., Kirmayer, S., Edri, E., Hodes, G., and Cahen, D. (2015). Rain on methylammonium lead iodide based perovskites: possible environmental effects of perovskite solar cells. *J. Phys. Chem. Lett.* 6, 1543–1547.

16. Levin, S.M., Goldberg, M., and Doucette, J.T. (1997). The effect of the OSHA lead exposure in construction standard on blood lead levels among iron workers employed in bridge rehabilitation. *Am. J. Ind. Med.* 31, 303–309.
17. Brunetti, B., Cavallo, C., Ciccioli, A., Gigli, G., and Latini, A. (2016). On the thermal and thermodynamic (in)stability of methylammonium lead halide perovskites. *Sci. Rep.* 6, 31896.
18. Leijtens, T., Eperon, G.E., Noel, N.K., Habisreutinger, S.N., Petrozza, A., and Snaith, H.J. (2015). Stability of metal halide perovskite solar cells. *Adv. Energy Mater.* 5, 1500963.
19. Rong, Y., Liu, L., Mei, A., Li, X., and Han, H. (2015). Beyond efficiency: the challenge of stability in mesoscopic perovskite solar cells. *Adv. Energy Mater.* 5, 1501066.
20. Babayigit, A., Ethirajan, A., Muller, M., and Conings, B. (2016). Toxicity of organometal halide perovskite solar cells. *Nat. Mater.* 15, 247–251.
21. Volans, G.N. (1987). Medical toxicology, diagnosis and treatment of human poisoning. *Trends Pharmacol. Sci.* 9, 267.
22. Florence, T.M., Lilley, S.G., and Stauber, J.L. (1988). Skin absorption of lead. *Lancet* 332, 157–158.
23. Dauvalter, V. (1955). Influence of pollution and acidification on metal concentrations in Finnish Lapland lake sediments. *Water Air Soil Pollut.* 85, 853–858.
24. Abate, A. (2017). Perovskite solar cells go lead free. *Joule* 1, 659–664.
25. Jellicoe, T.C., Richter, J.M., Glass, H.F.J., Tabachnyk, M., Brady, R., Dutton, S.E., Rao, A., Friend, R.H., Credgington, D., Greenham, N.C., and Böhm, M.L. (2016). Synthesis and optical properties of lead-free cesium tin halide perovskite nanocrystals. *J. Am. Chem. Soc.* 138, 2941–2944.
26. Im, J.H., Jang, I.H., Pellet, N., Gratzel, M., and Park, N.G. (2014). Growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$ cuboids with controlled size for high-efficiency perovskite solar cells. *Nat. Nanotechnol.* 9, 927.
27. Tétreault, N., Horváth, E., Moehl, T., Brillet, J., Smajda, R., Bungener, S., Cai, N., Wang, P., Zakeeruddin, S.M., Forró, L., et al. (2010). High-efficiency solid-state dye-sensitized solar cells: Fast charge extraction through self-assembled 3D fibrous network of crystalline TiO_2 nanowires. *ACS Nano* 4, 7644–7650.
28. Kang, D., Liu, Q., Chen, M., Gu, J., and Zhang, D. (2016). Spontaneous cross-linking for fabrication of nanohybrids embedded with size-controllable particles. *ACS Nano* 10, 889–898.
29. Chen, M., Gu, J., Sun, C., Zhao, Y., Zhang, R., You, X., Liu, Q., Zhang, W., Su, Y., Su, H., et al. (2016). Light-driven overall water splitting enabled by a photo-Dember effect realized on 3D plasmonic structures. *ACS Nano* 10, 6693–6701.
30. Yan, R., Chen, M., Zhou, H., Liu, T., Tang, X., Zhang, K., Zhu, H., Ye, J., Zhang, D., and Fan, T. (2016). Bio-inspired plasmonic nanoarchitected hybrid system towards enhanced far red-to-near infrared solar photocatalysis. *Sci. Rep.* 6, 20001.
31. Fu, P.P., Xia, Q., Hwang, H.M., Ray, P.C., and Yu, H. (2014). Mechanisms of nanotoxicity: generation of reactive oxygen species. *J. Food Drug Anal.* 22, 64–75.
32. Haruyama, J., Sodeyama, K., Han, L., and Tateyama, Y. (2015). First-principles study of ion diffusion in perovskite solar cell sensitizers. *J. Am. Chem. Soc.* 137, 10048–10051.
33. Sabba, D., Mulmudi, H.K., Prabhakar, R.R., Krishnamoorthy, T., Baikie, T., Boix, P.P., Mhaisalkar, S., and Mathews, N. (2015). Impact of anionic Br^- substitution on open circuit voltage in lead free perovskite ($\text{CsSnI}_{3-x}\text{Br}_x$) solar cells. *J. Phys. Chem. C* 119, 1763–1767.
34. Patrick, C.E., Jacobsen, K.W., and Thygesen, K.S. (2015). Anharmonic stabilization and band gap renormalization in the perovskite CsSnI_3 . *Phys. Rev. B* 92, 201205.
35. Wang, N., Zhou, Y., Ju, M.G., Garces, H.F., Ding, T., Pang, S., Zeng, X.C., Padture, N.P., and Sun, X.W. (2016). Heterojunction-depleted lead-free perovskite solar cells with coarse-grained B-y-CsSnI₃ thin films. *Adv. Energy Mater.* 6, 1601130.
36. Wu, B., Zhou, Y., Xing, G., Xu, Q., Garces, H.F., Solanki, A., Goh, T.W., Padture, N.P., and Sum, T.C. (2017). Long minority-carrier diffusion length and low surface-recombination velocity in inorganic lead-free CsSnI_3 perovskite crystal for solar cells. *Adv. Funct. Mater.* 27, 1604818.
37. Chung, I., Song, J.H., Im, J., Androulakis, J., Malliakas, C.D., Li, H., Freeman, A.J., Kenney, J.T., and Kanatzidis, M.G. (2012). CsSnI_3 : semiconductor or metal? High electrical conductivity and strong near-infrared photoluminescence from a single material. High hole mobility and phase-transitions. *J. Am. Chem. Soc.* 134, 8579–8587.
38. Xiao, Z., Zhou, Y., Hosono, H., and Kamiya, T. (2015). Intrinsic defects in a photovoltaic perovskite variant Cs_2SnI_6 . *Phys. Chem. Chem. Phys.* 17, 18900–18903.
39. Ju, M.G., Dai, J., Ma, L., and Zeng, X.C. (2017). Lead-free mixed tin and germanium perovskites for photovoltaic application. *J. Am. Chem. Soc.* 139, 8038–8043.
40. Ju, M.G., Chen, M., Zhou, Y., Garces, H.F., Dai, J., Ma, L., Padture, N.P., and Zeng, X.C. (2018). Earth-abundant nontoxic titanium(IV)-based vacancy-ordered double perovskite halides with tunable 1.0 to 1.8 eV bandgaps for photovoltaic applications. *ACS Energy Lett.* 3, 297–304.
41. Ming, W., Shi, H., and Du, M.H. (2016). Large dielectric constant, high acceptor density, and deep electron traps in perovskite solar cell material CsGeI_3 . *J. Mater. Chem. A* 4, 13852–13858.
42. Ke, W., Stoumpos, C.C., Zhu, M., Mao, L., Spanopoulos, I., Liu, J., Kontsevoi, O.Y., Chen, M., Sarma, D., Zhang, Y., et al. (2017). Enhanced photovoltaic performance and stability with a new type of hollow 3D perovskite FASnI_3 . *Sci. Adv.* 3, 8.
43. Yin, Y., Huang, Y., Wu, Y., Chen, G., Yin, W.J., Wei, S.H., and Gong, X. (2017). Exploring emerging photovoltaic materials beyond perovskite: the case of skutterudite. *Chem. Mater.* 29, 9429–9435.
44. Volonakis, G., Haghighirad, A.A., Milot, R.L., Sio, W.H., Filip, M.R., Wenger, B., Johnston, M.B., Herz, L.M., Snaith, H.J., and Giustino, F. (2017). $\text{Cs}_2\text{InAgCl}_6$: a new lead-free halide double perovskite with direct band gap. *J. Phys. Chem. Lett.* 8, 772–778.
45. Saparov, B., Hong, F., Sun, J.P., Duan, H.S., Meng, W., Cameron, S., Hill, I.G., Yan, Y., and Mitzi, D.B. (2015). Thin-film preparation and characterization of $\text{Cs}_3\text{Sb}_2\text{I}_9$: a lead-free layered perovskite semiconductor. *Chem. Mater.* 27, 5622–5632.
46. Slavney, A.H., Hu, T., Lindenberg, A.M., and Karunadasa, H.I. (2016). A bismuth-halide double perovskite with long carrier recombination lifetime for photovoltaic applications. *J. Am. Chem. Soc.* 138, 2138–2141.
47. Giustino, F., and Snaith, H.J. (2016). Toward lead-free perovskite solar cells. *ACS Energy Lett.* 1, 1233–1240.
48. Yang, B., Chen, J., Hong, F., Mao, X., Zheng, K., Yang, S., Li, Y., Pullerits, T., Deng, W., and Han, K. (2017). Lead-free, air-stable all-inorganic cesium bismuth halide perovskite nanocrystals. *Angew. Chem. Int. Ed.* 56, 12471–12475.
49. Xiao, Z., Du, K., Meng, W., Wang, J., Mitzi, D.B., and Yan, Y. (2017). Intrinsic instability of $\text{Cs}_2\text{In}(\text{I})\text{M}(\text{III})\text{X}_6$ (M = Bi, Sb; X = halogen) double perovskites: a combined density functional theory and experimental study. *J. Am. Chem. Soc.* 139, 6054–6057.
50. Xiao, Z., Du, K.Z., Meng, W., Mitzi, D.B., and Yan, Y. (2017). Chemical origin of the stability difference between copper(I)- and silver(I)-based halide double perovskites. *Angew. Chem. Int. Ed.* 56, 12107–12111.
51. Ju, M.G., Dai, J., Ma, L., and Zeng, X.C. (2017). Perovskite chalcogenides with optimal bandgap and desired optical absorption for photovoltaic devices. *Adv. Energy Mater.* 7, 1700216.
52. Zhang, T., Dar, M.I., Li, G., Xu, F., Guo, N., Gratzel, M., and Zhao, Y. (2017). Bication lead iodide 2D perovskite component to stabilize inorganic α - CsPbI_3 perovskite phase for high-efficiency solar cells. *Sci. Adv.* 3, 9.
53. McMeekin, D.P., Sadoughi, G., Rehman, W., Eperon, G.E., Saliba, M., Hörantner, M.T., Haghighirad, A., Sakai, N., Korte, L., Rech, B., et al. (2016). A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. *Science* 351, 151–155.
54. Ali, R., Hou, G., Zhu, Z., Yan, Q., Zheng, Q., and Su, G. (2018). Predicted lead-free perovskites for solar cells. *Chem. Mater.* 30, 718–728.
55. Nakajima, T., and Sawada, K. (2017). Discovery of Pb-free perovskite solar cells via high-throughput simulation on the K computer. *J. Phys. Chem. Lett.* 8, 4826–4831.
56. Dai, J., Ma, L., Ju, M., Huang, J., and Zeng, X.C. (2017). In- and Ga-based inorganic double perovskites with direct bandgaps for photovoltaic applications. *Phys. Chem. Chem. Phys.* 19, 21691–21695.

57. Zhao, X., Yang, J., Fu, Y., Yang, D., Xu, Q., Yu, L., Wei, S., and Zhang, L. (2017). Design of lead-free inorganic halide perovskites for solar cells via cation-transmutation. *J. Am. Chem. Soc.* **139**, 2630–2638.
58. Zhao, X., Yang, D., Sun, Y., Li, T., Zhang, L., Yu, L., and Zunger, A. (2017). Cu–In halide perovskite solar absorbers. *J. Am. Chem. Soc.* **139**, 6718–6725.
59. Sakai, N., Haghighirad, A.A., Filip, M.R., Nayak, P.K., Nayak, S., Ramadan, A., Wang, Z., Giustino, F., and Snaith, H.J. (2017). Solution-processed cesium hexabromopalladate(IV), Cs_2PdBr_6 , for optoelectronic applications. *J. Am. Chem. Soc.* **139**, 6030–6033.
60. Debbichi, L., Lee, S., Cho, H., Rappe, A.M., Hong, K.H., Jang, M.S., and Kim, H. (2018). Mixed valence perovskite $\text{Cs}_2\text{Au}_2\text{I}_6$: a potential material for thin-film Pb-free photovoltaic cells with ultrahigh efficiency. *Adv. Mater.* **30**, 1707001.
61. Pang, S., Zhou, Y., Wang, Z., Yang, M., Krause, A.R., Zhou, Z., Zhu, K., Padture, N.P., and Cui, G. (2016). Transformative evolution of organolead triiodide perovskite thin films from strong room-temperature solid–gas interaction between $\text{HPbI}_3\text{--CH}_3\text{NH}_2$ precursor pair. *J. Am. Chem. Soc.* **138**, 750–753.
62. Sun, Q., and Yin, W. (2017). Thermodynamic stability trend of cubic perovskites. *J. Am. Chem. Soc.* **139**, 14905–14908.
63. Castelli, I.E., Olsen, T., Datta, S., Landis, D.D., Dahl, S., Thygesen, K.S., and Jacobsen, K.W. (2012). Computational screening of perovskite metal oxides for optimal solar light capture. *Energy Environ. Sci.* **5**, 5814–5819.
64. Korbøl, S., Marques, M.A.L., and Botti, S. (2016). Stability and electronic properties of new inorganic perovskites from high-throughput *ab initio* calculations. *J. Mater. Chem. C* **4**, 3157–3167.
65. Schmidt, J., Shi, J., Borlido, P., Chen, L., and Botti, S. (2017). Predicting the thermodynamic stability of solids combining density functional theory and machine learning. *Chem. Mater.* **29**, 5090–5103.
66. Takahashi, K., Takahashi, L., Miyazato, I., and Tanaka, Y. (2018). Searching for hidden perovskite materials for photovoltaic systems by combining data science and first principle calculations. *ACS Photon.* **5**, 771–775.
67. Pilania, G., Balachandran, P.V., Kim, C., and Lookman, T. (2016). Finding new perovskite halides via machine learning. *Front. Mater.* **3**, 19.
68. Li, Z., Xu, Q., Sun, Q., Hou, Z., and Yin, W. (2018). Stability engineering of halide perovskite via machine learning. *ArXiv*, 1803.06042.
69. Lee, M.M., Teuscher, J., Miyasaka, T., Murakami, T.N., and Snaith, H.J. (2012). Efficient hybrid solar cells based on meso-structured organometal halide perovskites. *Science* **338**, 643–647.
70. Burschka, J., Pellet, N., Moon, S.J., Humphry Baker, R., Gao, P., Nazeeruddin, M.K., and Grätzel, M. (2013). Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* **499**, 316.
71. Xiao, Z., Cheng, B., Shao, Y., Dong, Q., Wang, Q., Yuan, Y., Wang, C., Gao, Y., and Huang, J. (2014). Efficient, high yield perovskite photovoltaic devices grown by interdiffusion of solution-processed precursor stacking layers. *Energy Environ. Sci.* **7**, 2619–2623.
72. Chen, M., Ju, M.G., Carl, A.D., Zong, Y., Grimm, R.L., Gu, J., Zeng, X.C., Zhou, Y., and Padture, N.P. (2018). Cesium titanium(IV) bromide thin films based stable lead-free perovskite solar cells. *Joule* **2**, 1–13.
73. Ávila, J., Momblona, C., Boix, P.P., Sessolo, M., and Bolink, H.J. (2017). Vapor-deposited perovskites: the route to high-performance solar cell production? *Joule* **1**, 431–442.