

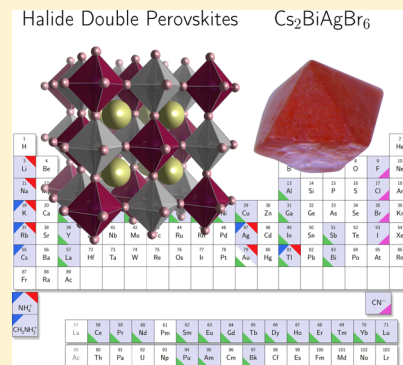
Toward Lead-Free Perovskite Solar Cells

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ABSTRACT: Since the first reports of solar cells with power conversion efficiencies around 10% in 2012, the science and technology of perovskite photovoltaics has been progressing at an unprecedented rate. The current certified record efficiency of 22.1% makes perovskites the first solution-processable technology to outperform multicrystalline and thin-film silicon. For this technology to be deployed on a large scale, the two main challenges that need to be addressed are the material stability and the toxicity of lead. In particular, while lead is allowed in photovoltaic modules, it would be desirable to find alternatives which retain the unique optoelectronic properties of lead halide perovskites. Here we offer our perspective on the most exciting developments in the materials science of new halide perovskites, with an emphasis on alternatives to lead. After surveying recent developments of new perovskites and perovskite-related materials, we highlight the potential of halide double perovskites. This new family of compounds constitutes uncharted territory and may offer a broad materials library for solar energy applications.



Solar cells based on halide perovskites are currently the fastest-growing photovoltaics (PV) technology in terms of research and development.^{1–3} The first report on the potential of halide perovskites in PV energy conversion appeared in 2009.⁴ In this study the authors employed the hybrid organic–inorganic halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ as a light-sensitizer in a dye-sensitized solar cell architecture and demonstrated a power conversion efficiency (PCE) of 3.8%. The capability of halide perovskites to operate not only as strong light absorbers but also as efficient electron and hole conductors was demonstrated in two ground-breaking works in 2012,^{5,6} which reported efficiencies of 10.9% and 9.7%, respectively. These works marked the beginning of a global research effort to push the performance of perovskite cells above the 20% efficiency mark, resulting in thousands of research papers published in this field during the past four years. Perovskite solar cells were soon due to break the efficiency records set by all other emerging PV technologies; at the time of writing, the highest certified efficiency is a stunning 22.1%,⁷ making perovskites the first solution-processable PV technology to have surpassed the efficiency of polycrystalline and thin-film silicon solar cells. During the past four years, research on perovskite-based PV expanded toward other important optoelectronic applications, such as for example light-emitting diodes,⁸ semiconductor lasers,⁹ and even optical cooling by photoluminescence upconversion.¹⁰

The element in common to most current research on perovskite-based photovoltaics and optoelectronics is the active material, primarily a hybrid organic–inorganic perovskite based on lead, halogens, and small organic molecules. The prototypical compound of this family is methylammonium

lead triiodide, MAPbI_3 with $\text{MA} = \text{CH}_3\text{NH}_3$, although in the most efficient solar cells MA is partly replaced by formamidinium, $\text{FA} = \text{CH}(\text{NH}_2)_2$.¹¹ MAPbI_3 crystallizes in the standard ABX_3 perovskite structure, as shown in Figure 1a. In this structure, Pb is at the center of regular PbI_6 octahedra, which in turn are connected in a three-dimensional corner-sharing network. The inorganic Pb–I network defines cuboctahedral cavities, each hosting one MA cation. At variance with standard perovskites, such as for example the mineral perovskite, CaTiO_3 , where the A, B, and X elements are in their formal oxidation states +2, +4, and –2, respectively, in halide perovskites one finds the formal charges CH_3NH_3^+ , Pb^{2+} , and I^- . At low temperature, MAPbI_3 crystallizes in an orthorhombic lattice with space group $Pnma$,^{12,13} see Figure 1a. With increasing temperature the system undergoes a first phase transition to a tetragonal lattice with space group $I4/mcm$ at 165 K and then becomes (pseudo)cubic at 327 K with space group $Pm\bar{3}m$. The topology of the perovskite structure is retained across these phase transitions; in fact, the structural changes are associated with a progressive suppression of octahedral tilts and the thermal activation of the spinning and tumbling of the MA cations.^{12–14}

MAPbI_3 exhibits a number of remarkable properties that make it ideal for optoelectronics applications. It is a direct-gap semiconductor, with a band gap of 1.6 eV at room temperature,¹⁵ very near the optimal Shockley–Queisser gap for single-junction solar cells (1.43 eV). It is a strong light

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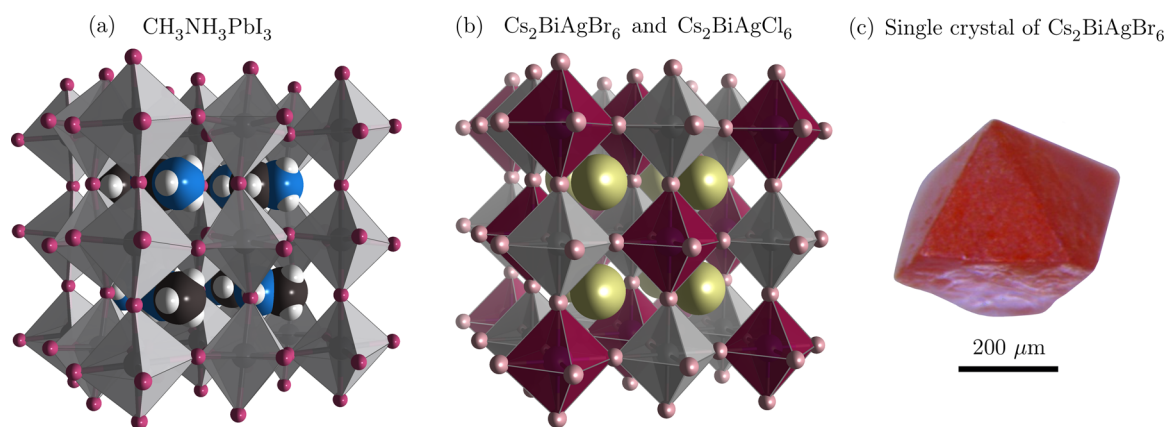


Figure 1. (a) Polyhedral model of MAPbI₃ in the low-temperature orthorhombic phase. PbI₆ octahedra are in gray; the I anions are brown; and the large spheres in the cavities represent the CH₃NH₃⁺ cations (N is blue, C is black). (b) Polyhedral model of Cs₂BiAgBr₆ in the room-temperature cubic phase. Cs is in yellow, and Br is pink; the BiBr₆ and AgBr₆ octahedra are in dark red and gray, respectively. (c) Photograph of a single crystal of Cs₂BiAgBr₆ (courtesy of A. A. Haghighirad, University of Oxford).

absorber, with an absorption coefficient $\alpha = 5 \times 10^4 \text{ cm}^{-1}$ in the red (1.7 eV), about 25 times higher than that in silicon and even superior to that of GaAs.¹⁶ The absorption onset is extremely sharp, with an Urbach energy as small as 13 meV and comparable (though slightly higher) to that of GaAs.^{16–18} The photogenerated electrons and holes are long-lived¹⁹ and exhibit diffusion lengths as long as 1 μm.^{20–22} In addition, the electron and hole effective masses are small and balanced,²³ leading to efficient ambipolar transport. These properties also enable photon recycling in MAPbI₃,²⁴ that is, the dissipationless absorption and emission of photons within the sample. This effect leads to an optimal utilization of solar photons within the active layer. Given their outstanding properties, MAPbI₃ and related compounds can be considered as the “first high-quality halide semiconductors”.²⁵ The unique optoelectronic properties of lead halide perovskites are even more surprising when considering that these films are routinely prepared by inexpensive solution-processing routes. The ease of fabrication makes halide perovskites ideally suited for scaling up the production using ink-based printing or spray-coating techniques.

The perovskite structure naturally lends itself to combinatorial chemistry. Following the development of solar cells based on MAPbI₃, many studies focused on the optimization of the materials by testing alternatives for the organic and metal cations as well as for the halides.^{11,26,27} Successful examples of materials optimization include solar cells based on solid solutions of FAPbI₃ and MAPbBr₃,²⁸ mixes of FA/Cs and I/Br,²⁹ triple-cation configurations such as Cs/MA/FA,³⁰ and perovskite–perovskite tandem devices employing Sn/Pb mixes.³¹ Interestingly, only MAPbI₃ forms a stable perovskite phase at room temperature, although mixtures of FA and Cs, Cs and MA, or MA and FA also yield crystal phases that are stable at room temperature. By tuning the compositions in the solid solutions it is therefore possible to identify “sweet spots” with good stability and high PV efficiency.

As current research on perovskite photovoltaics is rapidly approaching the theoretical efficiency limit for single junction solar cells, it is natural to ask what stands between the research in the laboratories and the deployment of this technology on a large scale. It is clear by now that the main outstanding issue is the tendency of these materials to degrade under exposure to moisture, heating, or prolonged illumination in air.³² This issue

has partly been addressed via compositional engineering;^{28–30} however, it still remains to be seen whether it will be possible to extend the lifespan of perovskite solar cells from several weeks to several tens of years. The second possible issue is the presence of Pb in the perovskite crystal. This does not pose a problem if Pb remains contained within the PV module; however, lead-based perovskites tend to release PbI₂ as a degradation product, which is toxic. Human exposure to lead is harmful to the nervous and reproductive systems and to the hematopoietic and renal organs, mainly as a result of increased oxidative stress.³³

One viable option for reducing the hazards of Pb exposure is to develop effective encapsulation strategies. In order for commercial solar panels to last for more than 25 years, the modules have to be extremely well encapsulated against moisture and oxygen ingress. In the most robust encapsulation protocols this is typically achieved by laminating the modules between two sheets of glass and polymer foil, followed by careful edge sealing. Furthermore, at the end of the module lifetime, it is important to ensure that all materials be recycled, as already happens for commercial thin-film PV technologies such as CdTe and CIGS. In practice, Pb is allowed in PV modules because solar panels are exempted from legislation such as the European Restriction on Hazardous Substances (RoHS).³ This exemption enables the continued use of existing PV modules, which also contain a significant amount of Pb.

Pb is allowed in PV modules, but it would be preferable to find an alternative.

In addition to improving the encapsulation of perovskites, another option is to replace Pb altogether in these materials. Alternatives to lead must fulfill very stringent criteria in order to match the performance of lead-halide perovskites. For example, the new compounds must exhibit excellent optoelectronic properties, comparable to the best inorganic semiconductors such as GaAs;²⁵ this requires direct band gaps for strong light absorption and photon recycling, as well as very small and balanced effective masses for efficient ambipolar transport. Furthermore, the new compounds should be defect-tolerant as is the case for MAPbI₃,³⁴ so as to suppress nonradiative

recombination channels. Finally, the new compounds should ideally be processable from solution in order to be competitive with established PV technologies. Taken together, these requirements render the elimination of Pb from perovskite solar cells a formidable scientific challenge.

The most obvious choice for Pb replacement is to use another group 14 metal, such as Sn or Ge. This would be a natural development, especially because the very first organic–inorganic halide perovskites used in optoelectronic devices were based on Sn.³⁵ From a fundamental standpoint, Sn-based halide perovskites constitute very promising materials for optoelectronic applications, owing to their optical band gaps in the red/infrared and good charge-carrier mobilities.²⁶ In 2012, the Sn-based perovskite CsSnI₃ was successfully employed as the inorganic hole-transporter in solid-state dye-sensitized solar cells.³⁶ In 2014, solar cells based entirely on the organic–inorganic Sn halide perovskites CH₃NH₃SnI₃³⁷ and CH₃NH₃Sn(I_{1-x}Br_x)₃³⁸ were demonstrated, with energy conversion efficiencies of 6.4% and 5.73%, respectively. Despite their proven potential, Sn-based perovskites are prone to self-doping effects and structural instabilities, owing to the known tendency of Sn²⁺ to oxidize into Sn⁴⁺; as a result, organic–inorganic perovskites based on Sn tend to degrade rapidly upon exposure to ambient air, and the device fabrication requires processing in nitrogen-filled glove-boxes.^{37,38} Furthermore, it is unclear whether Sn would be a safer alternative to Pb, because one of the degradation products, SnI₂, may be as harmful as its lead counterpart PbI₂.³⁹ Recent progress in this direction includes the stabilization of Sn in mixed Sn/Pb perovskites such as FA_{0.75}Cs_{0.25}Sn_{0.5}Pb_{0.5}I₃.³¹

These considerations raise a fundamental question: is it possible to completely replace Pb in perovskites solar cells by nontoxic elements, without compromising efficiency and stability, or is it the case that Pb is absolutely essential? In an attempt to answer this question, two recent computational studies screened all possible hypothetical halide perovskites that can be generated via homovalent replacement of Pb.^{40,41} In ref 40, the authors investigated the electronic structure of hypothetical CsB²⁺X₃ perovskites with X = Cl, Br, I using the low-temperature orthorhombic phase of CH₃NH₃PbI₃ as a starting template. For the metal cations B²⁺, the authors considered all possible elements which form dihalide salts, yielding more than a hundred unique compounds. This study revealed that no other metal cation is able to match the unique optoelectronic properties of Pb- and Sn-based perovskites, such as direct band gaps in the visible and low electron and hole effective masses. In ref 41, the authors performed a high-throughput search for stable ABX₃ perovskites using the high-temperature cubic structure as a starting template. Even after considering more than 32 000 hypothetical perovskites, the authors found that the only halide perovskites showing promise for PV applications were precisely compounds based on Pb, Sn, or Ge. Both these studies support the notion that halide perovskites based on Pb or Sn are truly unique in terms of optoelectronic properties.

In an attempt to stabilize Sn-based perovskites, several groups reported Sn-based halide perovskite derivatives with general composition A₂SnX₆, for example Cs₂SnI₆,^{42,43} Cs₂Sn(I,Br)₆,⁴⁴ and Cs₂SnX₆ with X = Cl, Br, I.⁴⁵ These compounds exhibit good stability in air and moisture, due to the presence of Sn in its stable +4 oxidation state. The crystal structures can be thought of as being derived from the cubic double perovskites Cs₂Sn₂X₆ by removing half of the octahedral Sn atoms, so as to

obtain a molecular salt formed by Cs⁺ cations and [SnI₆]²⁻ octahedra as anions, as shown in Figure 2. Because the Sn

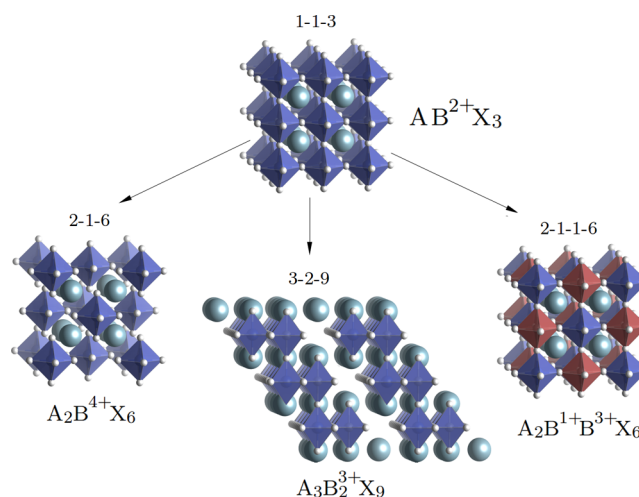


Figure 2. Schematic relation between the crystal structures of Pb-perovskites and lead-free perovskite derivatives. Moving from left to right, 2–1–6 compounds like Cs₂SnI₆ can be thought of as if obtained from lead halide perovskites by removing half of the B-site cations in a checkerboard pattern. In this case, charge neutrality requires the B-site cation to be in its +4 oxidation state. 3–2–9 compounds like Cs₃Sb₂I₉ can be imagined as derived from the perovskite at the top by removing one B-site cation every three, with all cations removed from planes defined by the <111> directions of the cubic perovskite crystal. In this case, the B-site cation must be in the +3 oxidation state in order to maintain charge neutrality. When the ionic radius of the A-site cation is large, the structure of these 3–2–9 compounds transforms into isolated face-sharing bi-octahedra, as in MA₃Sb₂I₉. 2–1–1–6 compounds like Cs₂BiAgCl₆ can be thought of as if obtained from the perovskite at the top by replacing every pair of adjacent B²⁺ cations by one B¹⁺ and one B³⁺ cation, so as to define a rock-salt arrangement of cations.

vacancies define a regular sublattice of the double perovskite structure, these compounds are termed “vacancy ordered” double perovskites, and indicated as Cs₂Sn⁴⁺□I₆ (□ stands for vacancy).⁴³ One intriguing feature of these materials is that, while they are reminiscent of molecular crystals, they exhibit unusually dispersive electronic band structures and direct band gaps which can be as low as 1.3 eV in the case of Cs₂SnI₆.⁴⁵

The concept of vacancy-ordered perovskites can also be used to describe new compounds with formula unit A₃B₂X₉, where A is a monovalent cation and B is a trivalent metal cation.^{46–49} These compounds can be thought of as perovskites of composition AB_{2/3}X₃, where one in three octahedral B³⁺ sites is vacant in order to maintain charge neutrality. The resulting structures are termed “two-dimensional layered perovskite derivatives” and crystallize in the *P3m1* space group (Figure 2). In these compounds, Pb²⁺ is replaced by Sb³⁺ or Bi³⁺, e.g., as in Cs₃Sb₂I₉⁴⁶ and Rb₃Sb₂I₉.⁵⁰ For large A-site cations these structures can transform into zero-dimensional dimers of face-sharing BX₆ octahedra (space group *P6₃/mmc*), for example, as in MA₃Sb₂I₉⁴⁸ and MA₃Bi₂I₉.⁴⁷ All these compounds have band gaps around 2.1 eV and exhibit enhanced air stability as compared to MAPbI₃. Mesoscopic heterojunction solar cells were reported for Cs₃Bi₂I₉ (1.09% PCE),⁴⁷ Rb₃Sb₂I₉ (0.66% PCE),⁵⁰ and MA₃Bi₂I₉ (0.2% PCE);⁴⁹ while planar heterojunction devices were reported for MA₃Sb₂I₉ (0.5% PCE).⁴⁸

Table 1. Summary of Pb-Free Perovskites and Perovskite Derivatives^a

family	stoichiom.	compound	solut.	solid st.	gap (eV)	PCE (%)	ref
perovskite	1–1–3	MASnI ₃	×	×	1.20–1.35		26
		MASnI ₃	×		1.23	6.4	37
		MASn _{1-x} Pb _x I ₃ ^b	×	×	1.21–1.54		26
		MASnI _{3-x} Br _x		×	1.30–2.15	5.73	38
		FASnI ₃	×	×	1.41		26
		CsSnI ₃	×	×	1.30		26
vacancy-ordered	2–1–6	Cs ₂ SnI ₆	×		1.26	6.94 ^c	42
		Cs ₂ SnBr ₆	×		2.7	0.04 ^c	45
double perovskite		Cs ₂ SnCl ₆	×		3.9	0.07 ^c	45
		Cs ₂ Sn _{1-x} Te _x I ₆ ^d	×		1.25–1.59		43
two-dimensional perovskite	3–2–9	Cs ₃ Sb ₂ I ₉		× ^e	2.05		46
		Cs ₃ Bi ₂ I ₉	×		2.2	1.09	47
		MA ₃ Sb ₂ I ₉	×		2.14	0.5	48
		MA ₃ Bi ₂ I ₉	×		2.1	0.12	47
		MA ₃ Bi ₂ I ₉	×			0.2	49
		Rb ₃ Sb ₂ I ₉	×		2.1–2.24	0.66	50
double perovskite (elpasolite)	2–1–1–6	Cs ₂ BiAgBr ₆		×	1.95		54
		Cs ₂ BiAgBr ₆	×	×	2.19		55
		Cs ₂ BiAgBr ₆	×	×	1.9		58
		Cs ₂ BiAgCl ₆	×	×	2.77		55
		Cs ₂ BiAgCl ₆		×	2.2		56
		MA ₂ BiKCl ₆	×		3.04		57
(other)	1–2–7	AgBi ₂ I ₇	×		1.87	1.22	51
(other)	1–1–5	HDABiI ₅	×		2.1	0.027	53

^aWe indicate the family name, stoichiometry, chemical formula, synthetic method (from solution or solid-state synthesis), measured band gap, and power-conversion efficiency for those cases where devices have been reported. ^b $x = 0, 0.25, 0.50, 0.75, 1$. ^cUsed as a hole transporter in a dye-sensitized cell. ^d $x = 0, 0.1, 0.25, 0.5, 0.75, 0.9, 1$. ^eFabricated through evaporation.

Related lead-free compounds include AgBi₂I₇,^{51,52} for which solar cells with PCE of 1.22% were reported,⁵¹ and HDABiI₅, where HDA is the divalent organic cation 1,6-hexanediammonium.⁵³ Table 1 summarizes these recently reported lead-free perovskites and perovskites derivatives, together with the corresponding device efficiencies where available.

An alternative possibility to realize lead-free compounds retaining the conventional perovskite structure but without resorting to Sn is to explore heterovalent substitution of Pb²⁺ by pairs of B-site cations with formal oxidation states +1 and +3 (Figure 2). This possibility was recently investigated in four independent studies.^{54–57} These studies reported on the synthesis of novel “double perovskites” based on bismuth and monovalent metals. In particular, ref 56 reported the computational screening of the hypothetical perovskites Cs₂BB³⁺X₆, with B³⁺ = Bi, Sb; B = Cu, Ag, Au; X = Cl, Br, I. Many of these hypothetical compounds were predicted to exhibit promising optoelectronic properties, such as band gaps in the visible and low effective masses. The authors of this study also reported the synthesis and characterization of the new double perovskite Cs₂BiAgCl₆. In ref 54, the authors reported the synthesis and characterization of the related compound Cs₂BiAgBr₆, and ref 55 reported both Cs₂BiAgCl₆ and Cs₂BiAgBr₆. The first step toward Pb-free hybrid organic–inorganic double perovskites was demonstrated in ref 57, with the synthesis of (CH₃NH₃)₂KBiCl₆.

According to these initial investigations, the new halide double perovskites have indirect band gaps ranging from 1.8–2.2 eV (Cs₂BiAgBr₆)^{54,55,58} to 2.2–2.8 eV (Cs₂BiAgCl₆),^{55,56,58} exhibit strong luminescence in the visible, and have long recombination lifetimes (660 ns, ref 54). First-principles calculations indicate that the bottom of the conduction band

is predominantly of antibonding Bi-6p/halogen-p character, while the top of the valence band is associated with Ag-4d/halogen-p antibonding orbitals.⁵⁸ The effective masses calculated in ref 56 are relatively anisotropic, with the lightest electron masses comparable to those of CH₃NH₃PbI₃. Both Cs₂BiAgBr₆ and Cs₂BiAgCl₆ appear considerably more stable than Pb-based perovskites in ambient air. For example, the X-ray diffraction pattern of Cs₂BiAgCl₆ does not show any noticeable changes after 3 weeks in ambient air;⁵⁶ furthermore, degradation in Cs₂BiAgBr₆ is observed only upon light exposure for 2 weeks.⁵⁵

Pb-free double perovskites will be a promising new research direction in perovskite PV and halide-based optoelectronics.

The structure of Cs₂BiAgBr₆ is shown in Figure 1b. At room temperature, this compound crystallizes in a face-centered cubic structure with space group *Fm* $\bar{3}$ *m*. The Bi and Ag cations alternate along the [100], [010], and [001] directions, so that the BiAg sublattice defines a rock-salt structure as in NaCl. This compound can be understood as a cubic perovskite with a doubled unit cell, that is, a “double perovskite”. Bi³⁺Ag¹⁺ double perovskites were obtained either by solution processing or via solid-state reaction,^{54–56,58} with the samples prepared from solution exhibiting higher phase purity.⁵⁵ The solution-based synthesis involves moderate temperatures (<150 °C) and yields a polycrystalline material upon cooling to room temperature. The resulting compound consists of octahedron-shaped crystals with sizes ranging from 0.1 mm⁵⁶ to 4 mm,⁵⁴ depending on the

1 H																	2 He	
3 Li	4 Be																	10 Ne
11 Na	12 Mg																	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 Ac																
NH ₄ ⁺																		CN ⁻
CH ₃ NH ₃ ⁺		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

Figure 3. Elements forming halide double perovskites (elposolites) with composition $A_2BB^3X_6$. An element is colored in light blue if at least one compound with elposolite structure containing that element has been synthesized. The triangular color tag specifies the site occupied by the element, according to the legend at the top. The compounds used to generate the table are described in refs 57 and 59–74. Only structures that crystallize in the space group $Fm\bar{3}m$ at room temperature have been considered for this table. The element Au is half-colored because it exists only in the compounds $A_2Au_2X_6$ with $A = Rb, Cs$ and $X = Cl, Br, I$. The structure of these compounds is obtained from the standard double perovskite by alternating compressed and elongated AuX_6 octahedra.⁷⁵

cooling rate. Figure 1c shows a photograph of a small single crystal of $Cs_2BiAgBr_6$, with its characteristic dark red color indicating a band gap in the visible.

While Pb-free double perovskites are only making their debut in solar energy research, related compounds have been known for many years under the name of “elposolites”. Elposolite is the name of the mineral K_2NaAlF_6 , first discovered in El Paso County, Colorado. Nowadays, synthetic elposolites find applications as scintillators for the detection of γ -rays, X-rays, and neutrons. For example, the most-studied elposolite scintillator is $Cs_2LiYCl_6:Ce^{3+}$, that is, a Cs_2LiYCl_6 elposolite crystal doped with Ce^{3+} impurities (typically 0.1%) on the $B^{3+} = Y$ site. This system has a very wide band gap (>6 eV), and the Ce^{3+} 4f and 5d states are located within the gap. Electrons and holes generated by ionizing radiation can form self-trapped excitons at the impurity sites, and the material scintillates upon radiative recombination.⁷⁶ This compound is also employed in the detection of thermal neutrons, by exploiting the high neutron absorption cross section of 6Li and the reaction ${}^6Li(n,\alpha)$.

A survey of the literature on elposolites shows that these compounds offer immense opportunities in terms of combinatorial chemistry. Already in 1982, for example, 234 cubic or tetragonal halide elposolites structures were known.⁷⁷ A more recent review suggests that at least 350 different elposolites have been synthesized.⁷⁸ In Figure 3 we highlight all the elements of the periodic table which belong to known halide elposolites.^{57,59–74} A simple count indicates that 7 elements are found as A-site cations, 8 elements can occupy the B^+ sites (including ammonium and methylammonium), 34 elements are found as B^{3+} cations, and 5 elements can occupy the X sites (including the cyanide CN^-). A straightforward multiplication of these numbers yields a stunning 9520

combinations. Following Goldschmidt’s rules,⁷⁹ we must expect that the majority of these combinations will correspond to unstable compounds; however, even within the pessimistic scenario that only 10% of these 9520 combinations are amenable to synthesis, we would still be facing over 900 possible compounds, out of which more than 600 compounds have never hitherto been investigated. These simple considerations suggest that the new halide double perovskites $Cs_2BiAgCl_6$, $Cs_2BiAgBr_6$, and $(CH_3NH_3)_2KBiCl_6$ may be only the tip of the iceberg, and that an entire new family of semiconductors may be waiting to be discovered. The computational screening of more than 600 hypothetical halide double perovskites represents a demanding task, but it certainly is within the reach of today’s computational capabilities.⁸⁰ This suggests that ab initio computations are ideally positioned to spearhead the search for new semiconducting perovskites.

Ab initio computations are ideally positioned to spearhead the search for new semiconducting perovskites.

Much work remains to be done in order to assess the potential of lead-free halide perovskites. For example, working solar cells based on $Cs_2BiAgBr_6$ have not been reported to date. This is largely due to the difficulty in developing a synthetic route to obtain uniform thin films of the correct phase and composition. The development of effective synthesis methods constitutes a priority for current and future research in this area. Another important limitation of the recently reported halide double perovskites is their indirect band gap. If lead-free materials are to match the unparalleled performance of their Pb-based counterparts, it will be important to devise strategies

in order to engineer a direct band gap with a strong oscillator strength for optical transitions. Finally, it will be critical to see how these new compounds and related low-gap double perovskites will perform in a solar cell under standard operating conditions.

These and many other challenges will have to be addressed before these new materials become competitive alternatives, but with some optimism we anticipate that double perovskites will be a promising new research direction in perovskite PV and halide-based optoelectronics. Could it be that the road toward safe and environmentally friendly solar energy eventually leads to El Paso?

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