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DROP-IT report
State-of-the-art Pb-free perovskite materials and devices

PREFACE

Within this report, we review the state-of-the-art lead-free perovskite materials. The first part contains most promising materials that have been studied to-date, experimentally and theoretically, and the second part focus on their application for opto-electronic devices, such as solar-cells, light-emitters and photo-catalysts. We provide detailed tables with the main features of the materials (Tables I-IV), their synthesis routes and electronic properties (*i.e.* electronic band gap: E_g and charge carrier effective masses: m_e, m_h), and the key parameters for their device performance (Tables V-VII). In terms of materials, we include the following Pb-free compound classes: ABX_3 halide single perovskites, $A_2BB'X_6$ halide double perovskite, A_2BX_6 vacancy ordered halide double perovskite, and the $A_3B_2X_9$ 2D perovskite derivatives (also referred to as a type of vacancy ordered double perovskites) [1]. (We do not include nano-crystal synthesis processes.) In terms of opto-electronic devices we include solar-cells, light-emitting diodes, and photocatalysts.

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1 MATERIALS

1.1 ABX_3 - Perovskite

A perovskite crystal of the form ABX_3 is the simplest form of a perovskite structure, and is consisted of a network of corner sharing BX_6 octahedra. A is typically a monovalent organic or inorganic cation; B is a divalent metal and X is a halide anion. Among different Pb-free perovskites, Sn based and Ge based perovskites can form the conventional ABX_3 perovskite structure. The typical attained space group is the Pm-3m. Popular example of Sn based perovskites are $CsSnI_3$, $MASnI_3$ and $FASnI_3$, ($MA = CH_3NH_3$, $FA = CH(NH_2)_2$) all of which exhibit direct electronic band gaps of 1.31, 1.20 and 1.41 eV respectively [2]. The main drawback of Sn based perovskites is related to the oxidation of Sn^{2+} to Sn^{4+}. Hence, the stability of the Sn-based materials is worse than the stability of their Pb-based counterparts. Typical Ge-based perovskites are $CsGeI_3$, $MAGeI_3$ and $FAGeI_3$ with direct band gap of 1.6, 1.9 and 2.2 eV respectively. Similar to the Sn-based perovskites, Ge-based perovskites also face stability issues due the oxidation of Ge^{2+}. However, it has been recently shown that alloys of Ge and Sn exhibit improved stability and narrower band gaps than pristine Ge- and Sn-based materials. For example, $CsSn_{0.5}Ge_{0.5}I_3$ alloys are stable compounds with a band gap of 1.5 eV [3]. Such alloying strategy has been also shown for the case of Pb and Sn alloys, for which the band gap is also known to decrease with respect to the pristine compounds and the materials remain stable [4].

Another promising route is the addition of large ethylenediammonium (*en*) cations within the $ASnI_3$ perovskite (A = MA, FA). This approach has been reported to introduce a large number of SnI_2 vacancies in the lattice. This type of structure is known as a hollow perovskite. [10, 113] Similar to Sn/Ge alloys, the stability of hollow perovskites is reported to be better than the stability of pristine Sn and Ge based perovskites. In Table I we report all ABX_3 perovskite structures that has been reported to-date, alongside the reported preparation method and their fundamental electronic properties (i.e. measured or calculated band gap, electron and hole effective masses).

Note for Tables I-IV: All reported experimental band gaps (i.e. band gaps for compounds with a reported synthesis method in Tables I-IV) are optical band gaps and all theoretical band gaps are electronic band gaps. Different materials have been synthesized using different methods which are mentioned in the table. Regarding the calculation of electronic band gap, different methods have been used theoretically to calculate the electronic band gaps. These methods include normal DFT calculations using the LDA, GGA, PBEsol exchange correlation functional. To include relativistic effect, spin orbit corrections (SOC) have been added in some studies. Tight binding methods are also used to estimate the electronic band gap. Also, to better capture the electronic band gap theoretically there are studies where advanced methods, such as using hybrid functionals or GW calculations, have been carried out. Specifically, among hybrid functionals, HSE and PBE0 have been used. The details of the theoretical methods are reported in Table I, II, III and IV. To avoid confusion between the normal DFT calculations and calculations with advanced method, DFT prefix have been used before the methods of normal DFT calculations.

TABLE I: Band gap, effective masses, preparation method and theoretical calculation techniques of Pb-free ABX_3 perovskites

Compounds	Synthesized (Yes/No)	Synthesis method	Theoretical calculations	E_g (eV)	m_e	m_h	Ref.
$MASnI_3$	Yes	Spin coating		1.2	-	-	[5]
•	Yes	Spin coating		1.3	-	-	[6]
•	Yes	Solvent engineering		1.3	-	-	[7]
•	Yes		HSE	1.2	0.10	0.12	[8]
•	Yes		DFT-PBE	0.8	0.17	0.11	[9]
$MASnBr_3$	Yes	Sequential evaporation		2.2	-	-	[7]
•	Yes		DFT-PBE	1.1	0.19	0.14	[9]
$MA_{0.9}Cs_{0.1}SnI_3$	Yes	Spin coating solvent engineering		1.4	-	-	[7]
{en}$MASnI_3$	Yes	Spin coating with SnF_2 additive		1.4	-	-	[10]
$FASnI_3$	Yes	Spin coating with SnF_2 additive		1.4	-	-	[5]
•	Yes	Spin coating with SnF_2 additive		1.4	-	-	[11]
•	Yes	Spin coating solvent engineering		1.4	-	-	[12]
•	Yes		DFT-PBE+SOC	0.9	0.02	0.05	[13]
$FASnI_2Br$	Yes	Spin coating solvent engineering		1.7	-	-	[12]
$FA_{0.25}MA_{0.75}SnI_3$	Yes	Spin coating solvent engineering		1.3	-	-	[11]
$FA_{0.5}MA_{0.5}SnI_3$	Yes	Spin coating solvent engineering		1.3	-	-	[11]
{en}$FASnI_3$	Yes	Spin coating with SnF_2 additive		1.5	-	-	[10]
•	Yes		DFT-PBE	1.4	-	-	[10]
$CsSnI_3$	Yes	Spin coating with SnI_2 additive		1.3	-	-	[14]
•	Yes	Spin coating with $SnCl_2$ additive		1.3	-	-	[15]
•	Yes		GW	1.4	-	-	[16]

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$CsSnI_2Br$	Yes	Spin coating with SnF_2 additive	1.4	-	-	[17]
$CsSnIBr_2$	Yes	Spin coating with SnF_2 additive	1.7	-	-	[17]
$MAGeI_3$	Yes	Spin coating	2.0	-	-	[18]
$CsGeI_3$	Yes	Spin coating	1.6	-	-	[18]
$CsSn_{0:5}Ge_{0:5}I_3$	Yes	Solid state reaction	1.5	-	-	[19]

1.2 $A_2BB'X_6$ Double Perovskite

Another type of perovskites that have been explored as potential Pb-free materials, is the so-called “double perovskites”. Double perovskites retain the conventional three-dimensional perovskite structure, but every two B^{2+} cite cations are substituted with two cations with formal oxidation states of +1 and +3. [20-23] The double perovskite structure has the general formula of $A_2BB'X_6$, which is simply a doubled standard ABX_3 perovskite structure. These compounds typically crystallize within a face-centered cubic $Fm\underline{3}m$ space group at room-temperature, and are particularly stable. For example, the cell parameter of the prototypical double perovskite $Cs_2AgBiBr_6$ is 11.25 Å [24], which is nearly two times larger than the unit cell parameter of $MAPbBr_3$ [25].

The double perovskite compounds which have been synthesized to-date, can be broadly divided into three categories, depending on their B’-site cation as follows: M^+/Bi^{3+}, M^+/In^{3+} and M^+/Sb^{3+}, with M a monovalent cation (i.e. Na, Ag, Cu, Ag, Au, In, Tl). We will discuss each kind of these double perovskites below, and within Table II we report all the double perovskite structures which have been synthesized and/or investigated theoretically.

Moving from the conventional Pb-based perovskite (e.g. $MAPbI_3$) structure to a double perovskite structure, it is important to maintain a similar electronic structure, which is the key factor underlying the remarkable opto-electronic properties of $MAPbI_3$, such as shallow defect states, long carrier life time, and strong absorption [26-28]. In particular, for $MAPbI_3$, the Pb^{2+} has a valence configuration of $6s^26p^0$. The valence band maximum (VBM) of $MAPbI_3$ is therefore made up of a mixture of the filled $6s^2$ and $5p^6$ states of Pb^{2+} and I^-, while the conduction band minimum (CBM) is made up of the vacant 6p state of Pb^{2+}. Apart from Pb^{2+} and Sn^{2+}, other main group metal cations like In^+, Tl^+, Sb^{3+} and Bi^{3+} can exhibit the $6s^26p^0$ electronic configuration. However, no environmentally friendly double perovskite with s^2p^0 valency at both the B and B' site, has been synthesized to-date, as shown in Table II.

1.2.1 M^+/Bi^{3+} – Double perovskite

Within this category, theoretical calculations and experiments have shown that halide double perovskites which have a noble metal as the monovalent B-site atom, exhibit an indirect band gap. [24, 34, 39, 50] For example, $Cs_2AgBiBr_6$ has an indirect band gap of 1.98 eV, with the lowest direct transition in the compound of 2.21 eV, which is lower than that of $MAPbBr_3$ (2.3 eV). [51] The presence of Ag 4d states and the Bi 6s states in the compound are known to be responsible for the indirect band gap of Cs_2AgBiX_6. These double perovskites can be synthesized using various techniques, and the preparation methods may introduce morphological and structural changes in the compounds, making them to exist in different forms *i.e.*, nanocrystals or as bulk compounds [52]. Structural modulation studies have demonstrated the possibility of tuning the band gap by applying pressure. For example, Li *et al*. reported that $Cs_2AgBiBr_6$ exhibits a narrower band gap by 22.3% through high-pressure treatment (*i.e.* 1.7 eV under 15 GPa) [53]. Overall, first-principles calculations have shown that the indirect electronic band gap of $Cs_2BB'X_6$, increases when moving up the halogen or the pnictogen column (i.e. replacing Bi with Sb as discussed below) in the periodic table. [30]

For all double perovskites in this category, the electron and hole effective masses calculated at the band edges usually exhibit an anisotropic behavior, with electron masses usually slightly more isotropic than the holes. The compounds are found to exhibit small carrier effective masses ranging between 0.1 and 0.4 m_e, which are close to the values of $MAPbI_3$. Halide double perovskites could exhibit tunable band gap and effective mass due to the flexibility in the variation of their chemical components. Finally, mixed alloys of double perovskites (*i.e.* mixing the B and B' cations) have also attracted interest, due to their ease of synthesis, low effective masses and tunable band gaps [54].

TABLE II: Band gap, effective masses, preparation method and theoretical calculation techniques of Pb-free $A_2BB'X_6$ perovskites

Compounds	**Synthesized (Yes/No)**	**Preparation method**	**Theoretical calculations**	**E_g (eV)**	**m_e**	**m_h**	**Ref.**
$Cs_2AgBiCl_6$	Yes	Solution process and precipitation		2.5	-	-	[29]
•	Yes		PBE0+SOC	2.7	0.34	0.63	[30]
•	Yes		DFT-GGA	1.9	-	-	[31]
•	Yes		DFT-PBEsol	1.8	-	-	[31]
•	Yes		DFT-LDA	1.7	-	-	[31]
$Cs_2AgBiBr_6$	Yes	Solution process and precipitation		2.0	-	-	[29]
•	Yes	Solution process		2.2	-	-	[32]
•	Yes	Vacuum sublimation		2.0	-	-	[33]
•	Yes		PBE0+SOC	2.3	0.48	0.57	[30]
•	Yes		HSE+SOC	1.9	-	-	[34]

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•	Yes		DFT-GGA	1.4	-	-	[31]
•	Yes		DFT-PBEsol	1.3	-	-	[31]
•	Yes		DFT-LDA	1.2	-	-	[31]
Cs_2AgBiI_6	Yes	Anion exchange reaction		1.8			[35]
•	Yes		PBE0+SOC	1.6	0.33	0.49	[30]
•	Yes		DFT-GGA	0.9	-	-	[31]
•	Yes		DFT-PBEsol	0.8	-	-	[31]
•	Yes		DFT-LDA	0.8	-	-	[31]
$Cs_2AuBiCl_6$	No		PBE0+SOC	1.6	0.37	0.50	[30]
$Cs_2AuBiBr_6$	No		PBE0+SOC	1.1	0.30	0.41	[30]
$Cs_2CuBiCl_6$	No		PBE0+SOC	2.0	0.23	0.66	[30]
$Cs_2CuBiBr_6$	No		PBE0+SOC	1.9	0.16	0.58	[30]
Cs_2CuBiI_6	No		PBE0+SOC	1.3	0.34	0.48	[30]
$Cs_2NaBiCl_6$	No		DFT-PBE+SOC	2.9	0.58	1.87	[36]
$Cs_2NaBiBr_6$	No		DFT-PBE+SOC	2.4	0.41	1.29	[36]
Cs_2NaBiI_6	No		DFT-PBE+SOC	1.7	0.28	0.58	[36]
•	Yes	Hydrothermal method		1.7	0.28	0.58	[37]
$(CH_3NH_3)_2AgBiBr_6$	Yes	Hydrothermal method		2.0	-	-	[38]
$(CH_3NH_3)_2AgBiI_6$	Yes	Solid state synthesis		2.0	-	-	[38]
•	Yes		GLLB-SC	1.9	-	-	[38]
$Cs_2InBiCl_6$	No		HSE+SOC	0.28	-	-	[39]
$Cs_2InBiBr_6$	No		HSE+SOC	0.36	-	-	[39]
$Cs_2TlBiCl_6$	No		HSE+SOC	1.28	-	-	[39]
$Cs_2TlBiBr_6$	No		HSE+SOC	0.71	-	-	[39]
$Cs_2AgTlCl_6$	Yes	Solid state synthesis		1.96	-	-	[39]
$Cs_2AgTlCl_6$	Yes		GW	1.87	-	-	[39]

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$Cs_2AgTlBr_6$	Yes	Solid state synthesis		0.95	-	-	[39]
$Cs_2AgTlBr_6$	Yes		GW	0.63	-	-	[39]
$(CH_3NH_3)_2TlBiBr_6$	Yes	Hydrothermal method		2.2	-	-	[40]
$(CH_3NH_3)_2KBiCl_6$	Yes	Hydrothermal method		3.0	-	-	[41]
$(CH_3NH_3)_2KBiBr_6$	Yes	Hydrothermal method		3.0	-	-	[41]
$Cs_2AgSbCl_6$	Yes		HSE	2.4	-	-	[42]
•	Yes	Hydrothermal method		2.6	-	-	[42]
•	Yes	Hydrothermal method		2.5	-	-	[43]
•	Yes		PBE0+SOC	2.6	0.42	0.70	[30]
$Cs_2AgSbBr_6$	Yes	Hydrothermal method		1.64	0.32	0.63	[44]
$Cs_2AgSbBr_6$	Yes		PBE0+SOC	1.9	0.32	0.63	[30]
Cs_2AgSbI_6	No		PBE0+SOC	1.1	0.22	0.52	[30]
$Cs_2AuSbCl_6$	No		PBE0+SOC	1.3	0.30	0.67	[30]
$Cs_2AuSbBr_6$	No		PBE0+SOC	0.7	0.22	0.56	[30]
Cs_2AuSbI_6	No		PBE0+SOC	0.0	0.15	0.42	[30]
$Cs_2NaSbCl_6$	No		DFT-PBE+SOC	3.0	0.56	1.62	[36]
$Cs_2NaSbBr_6$	No		DFT-PBE+SOC	2.4	0.39	1.09	[36]
Cs_2NaSbI_6	No		DFT-PBE+SOC	1.7	0.27	0.68	[36]
$Cs_2CuSbCl_6$	No		PBE0+SOC	2.1	0.48	0.71	[30]
$Cs_2CuSbBr_6$	No		PBE0+SOC	1.6	0.34	0.64	[30]
Cs_2CuSbI_6	No		PBE0+SOC	0.9	0.23	0.52	[30]
$Cs_2InSbCl_6$	No		HSE+SOC	2.1	0.48	0.71	[30]
$Cs_2InSbBr_6$	No		HSE+SOC	1.6	0.34	0.64	[30]
Cs_2InSbI_6	No		HSE+SOC	0.9	0.23	0.52	[30]
$(CH_3NH_3)_2AgSbI_6$	Yes	Solid state reaction		1.9	-	-	[45]
•	Yes		DFT-PBE	1.3	-	-	[45]

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$Cs_2AgInCl_6$	Yes		DFT-PBE	1.8	-	-	[46]
•	Yes		HSE	2.3	-	-	[47]
•	Yes		TB-mBJ	3.7	-	-	[46]
•	Yes	Hydrothermal method		3.5	-	-	[46]
$Rb_2AgInCl_6$	No		HSE	2.4	-	-	[48]
$Fr_2BiInBr_6$	No		PBE0	0.8	0.07	0.08	[49]
$(Cs/MA/FA)_2BiInBr_6$	No		PBE0	1.7-20	0.23	0.26	[49]

1.2.2 M^+/Sb^{3+} – Double perovskite

These materials in terms of electronic properties are very similar to the previous category, since Sb^{3+} and Bi^{3+}, have the same electronic configuration. Computational studies show that the electronic band gap of $Cs_2AgSbCl_6$ can be varied by an introduction of atomic disorder into its chemical structure [42], that involves the transposition of Ag^+ and Sb^{3+}. The transposed allotropes exhibit narrower band gaps compared to the pristine compound. These features can be attributed to the presence of local electric field between the oppositely charged Ag and Sb anti-site defects.

1.2.3 M^+/In^{3+} – Double perovskite

Direct band gaps can be achieved when replacing Bi^{3+} with In^{3+} in halide double perovskites. In addition, the electronic band-gap is predicted to decrease by replacing the Ag^+ with Cu^+. Particularly, Cu^+ based halide double perovskites such as $Cs_2CuInCl_6$ have been reported to exhibit a direct electronic band gap, which is smaller than those of the corresponding Ag^+ based compounds.[47, 55] The intriguing electronic band structure can be attributed to the close Cu 3d states, which forms antibonding hybridization with the halogen p states. However, DFT calculation shows that Cu^+ based halide double perovskites are typically energetically unfavorable compared to Ag^+ based halide double perovskites. This is ascribed to the higher energy level of Cu 3d orbitals and the smaller ionic radius of Cu^+ than that of Ag^+. However, there has been no Cu material synthesized to-date, most likely due to the intrinsic instability of Cu^+ [47].

Finally, there are many double perovskites in all three categories discussed above, that have an alkali metal, typically Na, K or Rb, as monovalent cation at the B-site. These perovskites, exhibit large band gaps ($E_g > 3$ eV) and at non-dispersive electronic bands due to the ionic nature of the alkali metals, making these compounds not promising candidates for opto-electronic applications. [56, 57] In fact, these compounds have been widely studied since the early seventies as promising scintillators. As such, within this report we do not further include these compounds.

1.3 A_2BX_6 - Vacancy ordered double perovskite

The introduction of B site vacancy into the typical double perovskite creates a different series of compounds that are widely known as vacancy ordered double perovskites (A_2BX_6), such as Cs_2SnI_6 and Cs_2TiBr_6. Like double perovskites, the structure is derived from the conventional perovskites by doubling the ABX_3 unit cell along all three crystallographic axes and then removing every-other B-site cation. These structures also share the same space group Fm-3m as the typical double perovskites. These compounds typically exhibit good stability in air and moisture. This is true for Sn-based compounds as well, due to the presence of Sn in its stable +4 oxidation state. Interest in the vacancy-ordered double perovskite family was motivated by a 2014 study by Lee *et al.* [59], which demonstrated that Cs_2SnI_6 exhibits optical and electronic properties relevant for applications in photovoltaics. Cs_2SnI_6 compound exhibits intrinsic n-type electrical conductivity and other fascinating features such as a direct band gap and strong visible light absorption. The origin of the good conductivity in this compound has been hypothesized to stem from (a) the possession of dispersive conduction band states and (b) the presence of iodine vacancies.[60] A computational study of the defect chemistry in Cs_2SnI_6 suggested that the ambipolar doping and charge transport in Cs_2SnI_6 was due to the formation of n-type iodide vacancies/tin interstitials or p-type cesium vacancies [68]. Similar to the case of ABX_3 perovskites, the band gap and optical absorption of vacancy-ordered double perovskites are dictated by the electronic states of the B and X-site ions. As a consequence, band gaps of the iodide-based vacancy-ordered double perovskites are smaller than those of the bromide and chloride analogues. The magnitude and direct vs indirect nature of the band gap in vacancy-ordered double perovskites is further dictated by the interaction of the B-site with the halide ligands of the octahedra. While Cs_2SnI_6 possesses a direct band gap of 1.3 eV, replacing Sn with Te at the B-site yields a larger, indirect band gap of 1.59 eV for Cs_2TeI_6. [60] The larger magnitude of the band gap in Cs_2TeI_6 arises due to covalent interaction of the Te 5p states with the I 5p states that pushes the conduction band higher in energy.

Finally, another set of vacancy ordered double perovskites have been proposed that are based on either Ti^{4+} or Pd^{4+}. [66,69] These materials exhibit relatively low electronic band gaps, well-within the visible range, yet their application on solar-cell devices is questionable due to issues on both their stability and their ability to efficiently harvest light. [69] In Table III, we summarize all the vacancy ordered double perovskites that have been reported to-date.

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TABLE III: Band gap, effective masses, preparation method and theoretical calculation techniques of Pb-free vacancy ordered double perovskites

Compounds	Synthesized (Yes/No)	Preparation method	Theoretical calculations	E_g (eV)	m_e	m_h	Ref.
Cs_2SnI_6	Yes	Chemical bath deposition		1.5	-	-	[58]
•	Yes	Solution phase synthesis		1.3	-	-	[59]
•	Yes	Solution phase synthesis		1.3	0.48-0.92	1.32-2.75	[60]
Cs_2SnI_5Br	Yes	Two step spin coating		1.4	-	-	[61]
$Cs_2SnI_4Br_2$	Yes	Two step spin coating		1.4	-	-	[61]
$Cs_2SnI_2Br_4$	Yes	Two step spin coating		1.6	-	-	[61]
Cs_2SnIBr_5	Yes	Two step spin coating		2.4	-	-	[61]
Cs_2SnBr_6	Yes	Two step spin coating		2.9	-	-	[61]
•	Yes	Two step spin coating		2.7	-	-	[61]
•	Yes	Hydrothermal method		2.7	-	-	[62]
•	Yes		DFT-PBE	1.5	-	-	[62]
•	Yes		GW0	2.2	-	-	[62]
Cs_2SnCl_6	Yes	Hydrothermal method		3.9	-	-	[62]
•	Yes		DFT-PBE	2.2	-	-	[62]
•	Yes		GW0	3.2	-	-	[62]
$(CH_3NH_3)_2PtI_6$	Yes	Solution precipitation		1.35	-	-	[63]
$(CH_3NH_3)_2PtI_6$	Yes		HSE	0.92	0.31	0.99	[63]
$(CH(NH_2)_2)_2PtI_6$	Yes	Solution precipitation		1.37	-	-	[63]
$(CH(NH_2)_2)_2PtI_6$	Yes		HSE	1.27	0.43	1.61	[63]
Rb_2SnI_6	Yes	Solution precipitation		1.32	0.39	0.98	[64]
K_2PtI_6	No		HSE	1.20	0.40	1.15	[65]
Cs_2PdBr_6	Yes	Solution phase synthesis		1.6	0.53	0.85	[66]

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Cs_2PdI_6	No	Solution phase synthesis		0.86	0.47	1.37	[65]
Cs_2TeI_6	Yes	Solid state reaction		1.59	-	-	[60]
•	Yes		HSE+SOC	1.83	-	-	[60]
Cs_2TiI_6	Yes	Melt crystallization method		1.0	-	-	[67]
•	Yes		HSE+SOC	1.0	1.58	0.79-1.58	[67]
$Cs_2TiI_4Br_2$	Yes	Melt crystallization method		1.2	-	-	[67]
$Cs_2TiI_2Br_4$	Yes	Melt crystallization method		1.4	-	-	[67]
Cs_2TiBr_6	Yes	Melt crystallization method		1.8	-	-	[67]
•	Yes		HSE+SOC	1.9	1.79	0.9-1.79	[67]
$(NH_4)_2PtI_6$	Yes	Solid state reaction		1.8	-	-	[67]

1.4 $A_3B_2X_9$ - 2D perovskite derivatives

The concept of vacancy ordered perovskite can also be used to define another type of perovskites, which are also known as “two-dimensional (2D) perovskite derivatives”. The unit cell of this kind of perovskite can be obtained by taking three times the cubic ABX_3 perovskite and creating one vacancy. The general formula of these materials is $A_3B_2X_9$ where A is the monovalent cation, B a trivalent metal cation and X a halogen atom [70-73]. These structures are achieved by heterovalently replacing Pb^{2+} in the ABX_3 lattice by typically a trivalent pnictogen atom, like Sb^{3+} or Bi^{3+}. This leads to the formation of materials such as $Rb_3Sb_2I_9$ or $Cs_3Bi_2I_9$. [74, 75] Within this lattice, vacancies are ordered along [111] plane resulting in a 2D layer of BX_6 octahedra. [24, 30, 54] These structures usually crystallize in a P-3m1 space group at room temperatures. However, for large A-site cations like MA and FA can transform to zero dimensional dimers of face sharing octrahedra attaining usually the space group $P6_3/mmc$ as in the case of $MA_3Sb_2I_9$ and

$MA_3Bi_2I_9$. [76,77] The iodide compounds within this family of materials exhibit enhanced air stability and band gap ranges between 1.9-2.3 eV [70,71]. In Table IV, we report all the materials within the $A_3B_2X_9$ structure that have been reported to date.

TABLE IV: Band gap, effective masses, preparation method and theoretical calculation techniques of Pb-free 2D perovskite derivatives

Compounds	**Synthesized (Yes/No)**	**Preparation method**	**Theoretical calculations**	**E_g (eV)**	**m_e**	**m_h**	**Ref.**
$MA_3Bi_2I_9$	Yes	Spin coating		2.1	-	-	[78]
•	Yes	Two step evaporation		2.2	-	-	[79]
•	Yes	Solvent engineering		2.3	-	-	[80]
•	Yes		DFT-PBE	2.0	-	-	[81]
$MA_3Bi_2I_{9-x}Cl_x$	Yes	Spin coating		2.4	-	-	[76]
$MA_3Bi_2I_{9-x}S_x$	Yes	Spin coating		1.5	-	-	[76]
$MA_3Sb_2I_9$	Yes	Spin coating with HI additive		2.0	-	-	[82]
$Rb_3Sb_2I_9$	Yes	Spin coating with HI additive		2.1	-	-	[74]
$FA_3Bi_2I_9$	Yes	Spin coating with HI additive		2.1	-	-	[74]
$Cs_3Sb_2I_9$	Yes	Vapor assisted conversion		2.1	-	-	[75]
•	Yes		HSE	2.1	0.62	0.68	[75]
•	Yes	Spin coating with HI additive		2.0	-	-	[82]
$Cs_3Bi_2I_9$	Yes		DFT-PBE	2.0	-	-	[81]
•	Yes	Solid state reaction		1.9	-	-	[83]
•	Yes		HSE+SOC	2.3	-	-	[83]
$K_3Bi_2I_9$	Yes	Solid state reaction		2.1	-	-	[83]
•	Yes		HSE+SOC	2.2	-	-	[83]
$Rb_3Bi_2I_9$	Yes	Solid state reaction		2.1	-	-	[83]

•	Yes	HSE+SOC	2.2	-	-	[83]

2 DEVICES

2.1 Solar-cells

Halide perovskites are the fastest growing photovoltaics technology. The electronic and optical properties of Pb-based perovskites are perfect for solar cell application. In 2009, MAPbI$_3$ was first used as a light-sentisizer with power conversion efficiency of 3.8%. [130] Halide perovskite based solar cell came in 2012 using CsSnI$_3$ and MAPbI$_3$ films achieving efficiencies around 10%. [131-133] The highest efficiency of Pb-based perovskite for the solar cell application is 25.2% [134] (with an unpublished 25.5% from UNIST - certified by NREL Chart in September 2020). For Pb-based perovskite, there are mainly two challenges: poor stability and high toxicity.[135] Stability of the Pb-based perovskite has been enhanced by the use of 2D perovskite with improved device engineering and encapsulation. [136, 137] Up to now and without any doubt the most efficient solar cells are the Pb-based perovskites. However, a lot of research is going on Pb-free perovskite materials as an alternative for solar cell application. Why? Actually, mainly to tackle these two challenges, the toxicity of Pb and the fact that Pb based perovskites are not stable in air. In Table V all the Pb-free compounds synthesized until date for solar cell application, their power conversion efficiency (PCE, in %), open circuit voltage (V_{OC}, in V, is the maximum voltage available from a solar cell at zero current) and fabrication method has been shown. Among different categories of Pb-free materials, Sn-based ABX_3 type perovskite materials have the highest efficiency. This is due to their very similar electronic and optical properties as Pb material. The highest reported PCE of Sn based ABX_3 type perovskite is 6%. [84] Sn is a low toxic element but it degrades to SnO_2 after exposure to air.

TABLE V: Solar cell application of different Pb-free perovskites

Category	**Compound**	**PCE (%)**	**V_{oc} (V)**	**Fabrication method**	**Ref.**
ABX_3	$MASnI_3$	7.78%	0.66	Spin-coating with SnF_2 additive	[5]
	•	6.4%	0.88	Spin-coating	[5]
	•	5.44%	0.716	Spin-coating	[5]
	•	5.23%	0.68	Spin-coating	[84]
	•	3.89%	0.38	Spin-coating with SnF_2 additive and hydrazine vapour treatment	[7]
	•	3.15%	0.46	Spin-coating with SnF_2 additive	[85]
	•	2.14%	0.45	Spin-coating with solvent bathing	[86]
	•	1.94%	0.25	Spin-coating with SnF_2 additive	[87]
	•	1.86%	0.273	Low temperature vapour assisted solution deposition process	[88]
	•	1.7%	0.38	Thermal co-evaporation	[88]
	$MASnIBr_2$	5.73%	0.82	Spin-coating	[84]
	$MASnBr_3$	4.27%	0.88	Spin-coating	[84]
	•	1.12%	0.498	Vapour deposition	[89]
	$MASnIBr_{1.8}Cl_{0.2}$	3.1%	0.38	Drop casting	[91]
	$MA_{0.9}Cs_{0.1}SnI_3$	0.51%	0.49	Vapour assisted solution deposition process	[92]
	$MA_{0.9}Cs_{0.1}SnI_3$	0.3%	0.20	Spin-coating	[93]

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ABX_3	$FASnI_3$+ 4(aminomethyl)	10.9%	0.69	Spin-coating	[94]
	$FASnI_3$	10.1%	0.63	Spin coating with FAI, SnI_2 and SnF_2 additive	[95]
	•	6.75%	0.58	Spin-coating with Sn powder additive	[96]
	•	6.6%	0.48	Spin-coating with SnF_2 additive	[11]
	•	6.22%	0.48	Spin-coating with SnF_2 additive	[97]
	•	5.27%	0.38	Spin-coating with diethyl ether dripping and SnF2 additive	[98]
	•	4.8%	0.32	Spin-coating with pyrazine mediator and SnF2 additive	[98]
	•	3.12%	0.31	Spin-coating with SnF2 and HPA additive	[99]
	•	2.1%	0.24	Spin-coating	[100]
	•	1.72%	0.47	Spin-coating	[100]
	Br-doped $FASnI_3$	5.5%	0.414	Spin-coating with pyrazine mediator and SnF_2 additive	[101]
	$(FA)_{0.8}(Cs)_{0.2}SnI_3$	1.4%	0.24	Spin-coating solvent engineering	[93]
	$(FA)_{0.5}(MA)_{0.5}SnI_3$	5.92%	0.53	Spin-coating with SnF_2 additive	[11]
	$(FA)_{0.75}(MA)_{0.25}SnI_3$	8.12%	0.61	Spin-coating with SnF_2 additive	[11]
	•	7.2%	0.55	Spin-coating with SnF_2 additive and solvent vapour annealing	[103]
	$CsSnI_3$	4.81%	0.382	Spin-coating with SnI_2 additive	[14]
	•	3.83%	-	Spin-coating with SnF2 and piperazine additive	[104]
	•	3.56%	0.50	Spin-coating with SnCl2 additive	[15]
	•	3.31%	0.52	Spin-coating and annealing	[105]
	•	2.76%	0.43	Spin-coating with SnI_2 additive	[106]
	•	2.02%	0.24	Spin-coating with SnF_2 additive	[107]
	•	1.83%	0.17	Spin-coating with SnF_2 additive and hydrazine vapour treatment	[7]

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ABX_3	•	1.66%	0.20	Spin-coating with SnF_2 additive	[17]
	$CsSnI_3$	0.9%	0.42	Sequential evaporation and subsequent annealing	[107]
	$CsSn_{0:5}Ge_{0:5}I_3$	7.11%	0.63	Solid state reaction	[19]
	$CsSnI_{2:9}Br_{0:1}$	1.76%	0.222	Spin-coating with SnF_2 additive	[108]
	$CsSnI_2Br$	1.67%	0.29	Spin-coating with SnF2 additive	[17]
	$CsSnIBr_2$	3.2%	0.31	Sequential evaporation and subsequent annealing	[108]
	•	1.56%	0.31	Sequential evaporation and subsequent annealing	[17]
	$CsSnBr_3$	3.04%	0.37	Spin-coating with SnF_2 additive and hydrazine vapour treatment	[7]
	$CsSnBr_3$	3.04%	0.37	Spin-coating with SnF_2 additive and hydrazine vapour treatment	[7]
	$CsSnBr_3$	2.1%	0.41	Spin-coating with SnF_2 additive	[109]
	•	0.95%	0.41	Spin-coating with SnF_2 additive	[17]
	$CsSnI_3$ (QR)	12.96%	0.86	Spin-coating	[111]
	$CsSnBr_3$ (QR)	10.46%	0.85	Spin-coating	[111]
	$CsSnCl_3$ (QR)	9.66%	0.87	Spin-coating	[111]
	$MAGeI_3$	0.68%	-	-	[18]
ABX_3	•	0.20%	0.150	-	[18]
	$CsGeI_3$	0.11%	0.074	-	[112]
	{en}$MASnI_3$	6.63%	0.43	Spin-coating with SnF_2 additive	[113]
	{en}$FASnI_3$	7.14%	0.48	Spin-coating with SnF_2 additive	[10]
	•	7.23%	0.460	Spin-coating with SnF_2 additive	[10]
	•	8.9%	0.583	Spin-coating with SnF_2 additive	[10]
	{en]$FA_{0:78}GA_{0:22}SnI_3$	9.6%	0.619	Spin-coating with SnF_2 additive	[114]
	Cs_2SnI_6	0.96%	0.51	Thermal evaporation, annealing and phase change	[118]

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A_2BX_6	•	0.857%	0.52	Spin-coating	[119]
	•	1.47%	0.37	Two-step thin film deposition method	[61]
	•	0.47%	0.25	Chemical bath deposition	[58]
	Cs_2SnI_5Br	1.60%	0.44	Two-step thin film deposition method	[61]
	$Cs_2SnI_4Br_2$	2.03%	0.56	Two-step thin film deposition method	[61]
	$Cs_2SnI_2Br_4$	1.08%	0.58	Two-step thin film deposition method	[61]
	Cs_2SnIBr_5	0.002%	0.57	Two-step thin film deposition method	[61]
	Cs_2TiBr_6	3.28%	1.02	Two step vapor deposition	[120]
	•	2.26%	0.89	Two step vapor deposition	[120]
	$Cs_2SnI_3Br_3$	3.63%		Two step vapor deposition	[121]
$A_3B_2X_9$	$MA_3Bi_2I_9$	1.64%	0.81	Deposition and homogeneous transformation	[122]
	•	0.42%	0.67	Deposition and homogeneous transformation	[78]
	•	0.39%	0.81	Thermal evaporation, spin-coating and annealing	[79]
	•	0.36%	0.65	Solvent engineering	[123]
	•	0.31%	0.51	Spin coating	[124]
	•	0.259%	0.56	Spin-coating	[125]
	•	0.19%	0.35	Spin-coating	[76]
	•	0.12%	0.68	Spin-coating	[76]
	•	0.11%	0.72	Solvent engineering	[80]
	•	0.08%	0.69	Spin coating, gas assisted	[126]
	•	0.07%	0.66	Spin coating	[81]
	•	0.053%	0.84	Spin-coating	[127]
	$MA_3Bi_2I_{9-x}Cl_x$	0.003%	0.04	Spin-coating	[76]
	$MA_3Sb_2I_9$	2.04%	0.62	Spin-coating with HI additive	[82]
	•	0.5%	0.896	Spin-coating	[77]

	Sn^{4+}/ $MA_3Sb_2I_9$	2.70%	0.56	Spin-coating with chlorobenzene dripping	[128]
	$CsBi_3I_{10}$	0.40%	0.31	Spin-coating	[76]
	•	1.09%	0.85	Spin-coating	[76]
	•	0.02%	0.02	Spin-coating	[129]
$A_3B_2X_9$	$Cs_3Bi_2I_{10}$	0.40%	0.31	Spin-coating	[129]
	$Cs_3Sb_2I_9$	0.84%	0.60	Spin-coating with HI additive	[82]
	•	0.02%	0.02	Spin-coating	[129]
	•	<1%	0.307	Dual-annealing	[82]
	•	<1%	0.307	Dual-annealing	[82]
	$Rb_3Sb_2I_9$	0.66%	0.55	Spin-coating with toluene dripping	[74]
	$(NH_4)_3Sb_2I_9$	0.51%	1.03	Spin-coating with chloroform dripping	[130]

These perovskites are worse in stability than Pb-based perovskites even when encapsulated. In addition, the V_{OC} of these solar cells is much lower than Pb based perovskites. Hollow Sn-based perovskites, shown in Table V, have reached the highest PCE of 9.6%. [114]. The highest efficiency has been achieved by adding 1% ethylenediammonium (en) cation combining 20% guanidinium (GA). [114] The solar cell using the hollow perovskite shows better stability and efficiency. The solar cell efficiency of Ge based perovskite is inferior than Sn based perovskite and more Ge based perovskite is not stable. On the other hand, alloys of Ge and Sn show promising power conversion efficiency and better stability than Ge based perovskite. For instance, employing $CsSn_{0.5}Ge_{0.5}I_3$ allowed the fabrication of solar-cell devices with a PCE of 7.11%. [19] $CsSn_{0.5}Ge_{0.5}I_3$ based devices maintains 91% of initial efficiency after illumination in air for

100 hours. Mixture of Ge and Sn is a promising alternative if the power conversion efficiencies can be achieved higher than 10%.

Double perovskite and vacancy ordered double perovskite are very stable under ambient conditions, yet the electronic band gaps of the synthesized double perovskites range from 2 eV to 3.4 eV (see Table II) which is too large for single junction photovoltaics. The highest PCE obtained for double perovskite is for $Cs_2AgBiBr_6$ which is 2.84%. [114] The Sn in vacancy ordered double perovskite is +4 oxidation state, hence these perovskites structures are most stable among Sn-based perovskites. Vacancy ordered double perovskite structures, have achieved PCE of 3.63% by employing the mixed halide $Cs_2SnI_3Br_3$ compound. $A_3B_2X_9$ 2D perovskite derivatives have also been employed for solar cell application. Although these materials are quite stable in air, the achieved PCE is relatively low. Highest efficiency obtained to-date for 2D perovskite derivatives is 2.70% [128] obtained with Sn doped $MA_3Sb_2I_9$.

Finally, keeping in mind multi-junction device architectures, Sn-based perovskite are key components as low-band gap alloys useful for the design perovskite-perovskite based tandem solar cells. These efficient tandem solar cells cannot be obtained solely from lead-based perovskites (see Ref. 139 and all the literature contained therein). In Table V, we show all the synthesized Pb-free perovskite materials that have been reported, including their PCEs, V_{OC} and fabrication methods.

2.2 Light emitting application

Over the last years, Pb-based metal halide perovskites have gained great research interest due to their high PLQY. Zhou *et al*. [140] achieved a record-high PLQY of 94.6%, by employing $MAPbX_3$ (X = Cl, Br, I) nanocrystals embedded polyvinylidene fluoride (PVDF) composite films. Though it seems that Pb-free materials can hardly compete with Pb-based perovskite for solar-cells due to their low PCE, in the case of LED applications Pb-free perovskites can become promising materials due to both their high photoluminescence quantum yield (PLQY) and their large tunability across the entire visible spectrum. [140-143]. In addition, similar to Pb-based halide perovskites, Pb-free based LEDs show excellent performance and are similarly prepared by low cost solution processes. Their narrowband emission from free excitons and their broadband emission from self-trapped excitons both show possibilities in LED applications. Electronic dimensionality, defect passivation and impurity doping are the key factors for achieving high efficiency luminescence.

Among different kinds of Pb-free perovskites, double perovskite and vacancy ordered double perovskite show significant PLQY. The highest PLQY has been achieved for Bi-doped $Cs_2(Ag_{0.6}Na_{0.4})InCl_6$ which is 86% [146]. Apart from the double perovskite, vacancy ordered double perovskite structures are also very promising for LED applications as detailed in Table VI. Finally, low PLQY materials also attracting researcher's attention to understand the trap states related PL quenching. Table VI, includes all the Pb-free perovskite materials synthesized till date for LED application. The emission peak (in nm), color of the LED, full width half maximum (FWHM, in nm) and photoluminescence quantum yield (PLQY, in %).

TABLE VI: Performance of LED application of different Pb-free perovskites

Category	Compounds	Emission peak (nm)	Color	FWHM (nm)	PLQY (%)	Ref.	Comment
ABX_3	$MASn(Br/I)_3$	667-945			<5.3%	[144]	Films

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	$CsSnBr_3$	670	dark red		2.1%	[145]	Nanocages
$A_2BB^{'}X_6$	$Cs_2(Ag_{0:6}Na_{0:4})InCl_6:Bi^{3+}$	565	white		86%	[146]	Powder
	$Cs_2Ag(In_{0.875}Bi_{0.125})Cl_6$	585	white		70.3%	[147]	Powder
	$Cs_2NaEuCl_6$	593	red		35%	[148]	Powder
	$Cs_2NaTbCl_6$	548	green		56%	[148]	Powder
	$Cs_2AgBiBr_6$	465		82	0.7%	[149]	NanoCrystals
	$Cs_2AgBiCl_6$	395		68	6.7%	[149]	NanoCrystals
A_2BX_6	Bi doped Cs_2SnCl_6	455	white	66	78.9%	[150]	Powder
	Sb doped Cs_2SnCl_6	602	white	101	37%	[151]	Powder
	Cs_2SnI_6	643-742		75	28%	[152]	Nanoplatelets
$A_3B_2X_9$	$Cs_3Bi_2Br_9$	410	blue	48	19.4%	[153]	Quantum Dots (QD)
	$Cs_3Bi_2Cl_9$	393	blue	59	26.4%	[153]	QD
	$Cs_3Sb_2Br_9$	410	blue	41	46%	[154]	QD
	$Cs_3Sb_2Cl_9$	370		52	11%	[154]	QD
	$Cs_3Sb_2I_9$	560		56	23%	[154]	QD
	$FA_3Bi_2Br_9$	437	blue		52%	[155]	QD
	$MA_3Bi_2Br_9$	430	blue	62	12%	[156]	QD
	$MA_3Bi_2(Cl,Br)_9$	422	blue	41	54.1%	[157]	QD

2.3 Photocatalytic application

The main requirements to have a promising photocatalytic material are the following: strong light absorption, high chemical stability in the presence of electrolyte, a suitable band edge position and the ability to efficiently transport charge carriers. In order to ensure that the photo generated electrons and/or holes are favoring the catalytic reaction, the materials' conduction band minimum (CBM) must be more negative and/or valence band maximum (VBM) must be more positive than the redox potential. Over the last few years, photocatalysis using Pb-based halide perovskites has been developing rapidly. In 2016, $MAPbI_3$ showed promising performance for photo-catalytic water splitting. [158] The H_2 evolution rate was measured at 57 µmol $g^{-1}h^{-1}$ with a splitting efficiency of 0.81 %. $MAPbI_3$ was stable at specific saturation solution where $[I^-] \leq [H^+]$ and the pH≤ -0.5. In 2018, Wang *et al.* [159, 160] proposed a heterostructure of $MAPbI_3/TiO_2/Pt$ and $MAPbI_3/Ta_2O_5/Pt$ with significant enhancement in H_2 evolution rate of 89-fold and 52-fold over MAPbI3/Pt. Regarding CO_2 reduction which is also very important to reduce the use of fossil fuel, perovskite materials make significant progress. In 2017, Xu et al., [161] performed research on $CsPbBr_3$ quantum dots for the photocatalytic reduction of CO_2 which show CO and CH_4 evolution rate of 58.7 and 29.6 µmol $g^{-1}h^{-1}$. Although Pb-based perovskites are potential candidate for photocatalyst, yet they are limited by their low chemical stability.

To ensure the long-term stability of photocathode and photoanode, as well as to avoid lead contamination in the solution, Pb free perovskites are an evident alternative to study carefully. In addition, wider the electronic band gap of the perovskite material better it is for photocatalysis application. So, it has been observed that double perovskite and 2D perovskite derivatives are particularly important suitable for photocatalytic application due to wider electronic band gap and more enhanced stability. In fact, calculations have shown that most synthesized to-date double perovskites have electronic band gaps that are suitable for the promotion of water splitting [162]. In Table VII all the Pb-free materials synthesized for photocatalysis application and their performance has been tabulated.

TABLE VII: Performance of photocatalytic application of different Pb-free perovskites. In parenthesis, the production time in hour

Category	Compounds	CO mol/g	CH_4 mol/g	H_2 mol/g	Ref.
$A_2BB'X_6$	$Cs_2AgBiBr_6$	105 (6h)			[52]
	$Cs_2AgBiBr_6$/RGO			489 (10h)	[163]
$A_3B_2X_9$	$Cs_3Sb_2Br_9$	510 (4h)			[164]
	$Cs_3Bi_2I_9$	77.6 (10h)	14.9 (10h)		[165]
	$MA_3Bi_2I_9$			169.21 (1h)	[166]
	$Cs_3Bi_{2x}Sb_{2-2x}I_9$			92.6 (1h)	[167]
	$Rb_3Bi_2I_9$	18.2 (10h)	17.0 (10h)		[165]
	$MA_3Bi_2I_9$	7.2 (10h)	9.8 (10h)		[165]

3 CONCLUSIONS

In conclusion, within this review of state-of-the-art Pb-free perovskite materials, we reported on the different Pb-free families of perovskites that have been proposed in order to tackle both Pb environmental impact and reduced materials stability. In addition, we show that the type of perovskite compound can be very different depending of the targeted application.

For solar cell applications, the power conversion efficiency achieved to-date, is not high for any double perovskite $A_2BB'X_6$, vacancy ordered double perovskites A_2BX_6 or 2D perovskite derivatives $A_3B_2X_9$. For Sn based perovskite the power conversion efficiency is significantly higher but at the same-time these compounds are intrinsically not stable in ambient conditions. Sn-Ge mixed structures has the potential to be important perovskite materials for solar-cell applications if the PCE can be increased further. Today, the perovskite ABX_3 has the best PCE with B=Sn. For various A, these materials reached these PCEs: $MASnI_3$

(7.78%), $FASnI_3$ (10.9%), $(FA)_{0.75}(MA)_{0.25}SnI_3$ (9.06%), $CsSnI_3$ (4.81%), $CsSn_{0.5}Ge_{0.5}I_3$ (7.11%) and $CsSnI_3$ (QR) (12.96%). All the other categories such as $A_2BB'X_6$, A_2BX_6, and $A_3B_2X_9$ have a reported PCE less than 4%. Finally, Sn-based perovskites due to their low electronic band -gap, can be the corner stone material opening the road for perovskite/perovskite tandem solar cells.

For LED application, Pb free perovskite materials in particular double perovskite and vacancy ordered double perovskite can be promising, in particular for white-light emission, due to their high photoluminescence quantum yield. Indeed, the categories $A_2BB'X_6$ (double perovskite) and A_2BX_6 (vacancy ordered double perovskite) show more than 75% of PLQY for the white color. However, for the different color than white the PLQY are also still high with more than 50% for the category $A_2BB'X_6$ and also $A_3B_2X_9$ (2D perovskite derivatives) respectively. More precisely, blue with B=Bi for $A_3B_2X_9$ and green with B=Na and B'=Tb for $A_2BB'X_6$.

Finally, for photocatalysis, Pb-free perovskite materials have a significant potential, though we are still at the very beginnings of the field. This is because the electronic band gap is higher and more stability is higher for Pb-free perovskite as compared to Pb-based perovskite. Especially, the material with B=Bi of the 2D perovskite derivatives ($MA_3Bi_2I_9$) exhibits an encouraging performance to produce H_2 per 1 hour. Indeed, $Cs_2AgBiBr_6$ and $Cs_3Bi_{2x}Sb_{2-2x}I_9$ are still almost 3.5 time and 2time smaller than the production per hour of $MA_3Bi_2I_9$.

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