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A review of structural, optical and stability properties of lead-free halide double perovskites

By
Mutukwa D

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- Introduction
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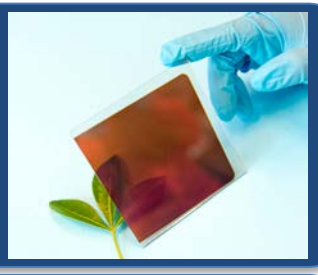
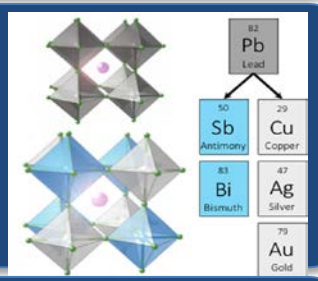
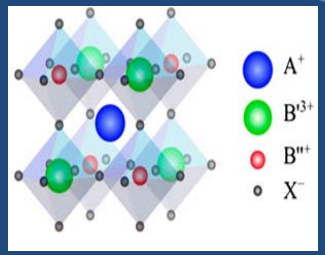
  - *Properties of Lead halide perovskites*
  - *Challenges of Lead halide perovskites*



- Heterovalent Substitution
  - *Substitution with a trivalent cation*
  - *Mixed valent substitution*



- Structure
  - *Halide double perovskites*



- Optical properties
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Introduction

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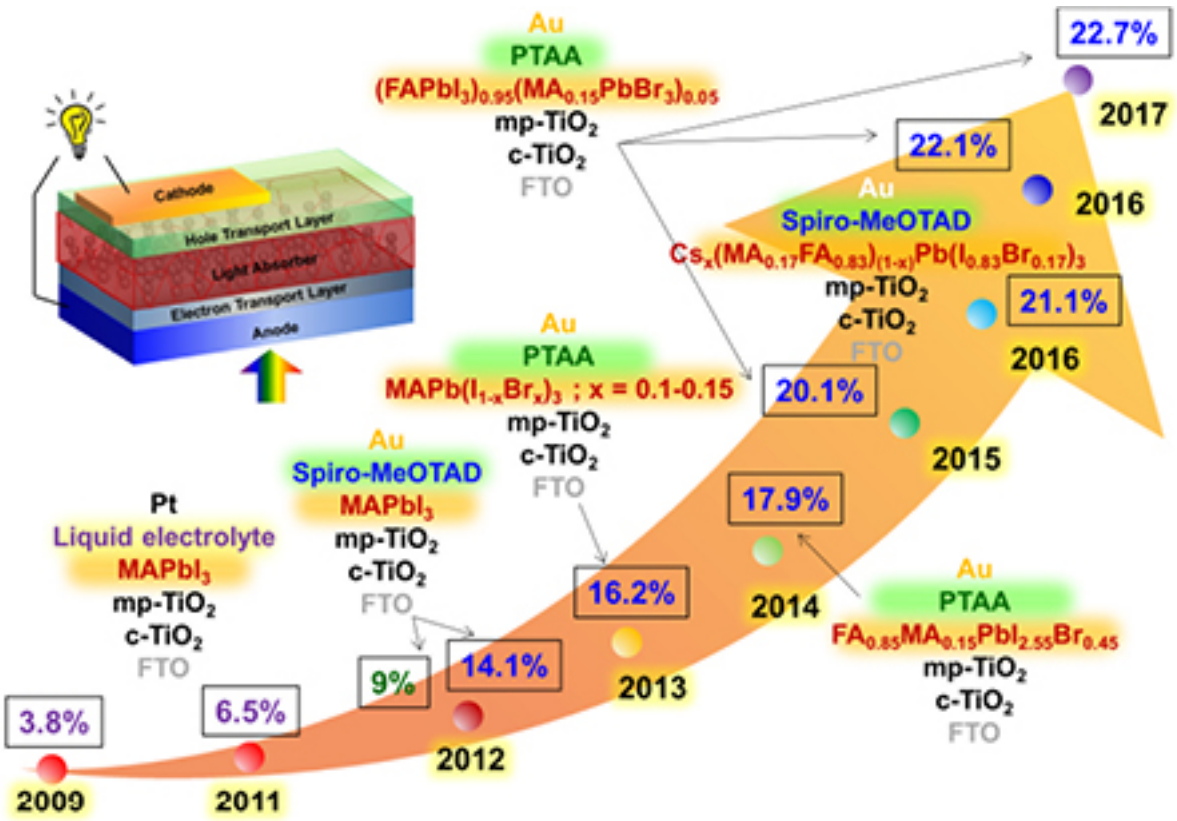
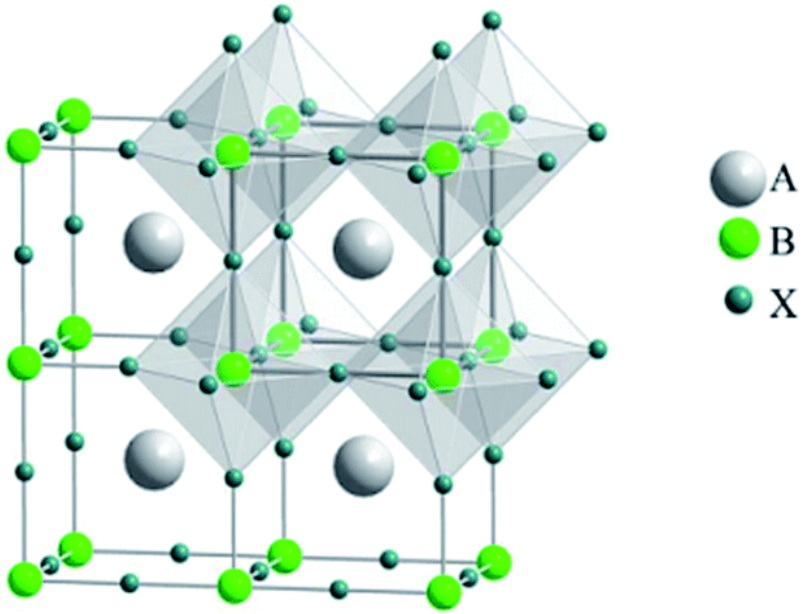
- Perovskite solar cells have sparked major research interest due to their remarkable performance[1,2].



Introduction



ABX_3 Perovskite structure. ©RSC 2016.

- Where, A is a monovalent cation (e.g. $CH_3NH_3^+$ (MA^+), $CH(NH_2)_2^+$ (FA^+), , Cs^+, K^+), B a divalent metal cation (e.g. Sn^{2+}, Pb^{2+}, Ge^{2+}) and X is halide anion (e.g. Cl^-, Br^-, I^-).

Introduction

Properties of perovskite materials:

- long charge diffusion length
- direct bandgap
- tunable bandgap
- low carrier recombination
- high carrier mobilities
- high molar extinction coefficient and strong absorption in the visible spectrum [3,4].

Introduction

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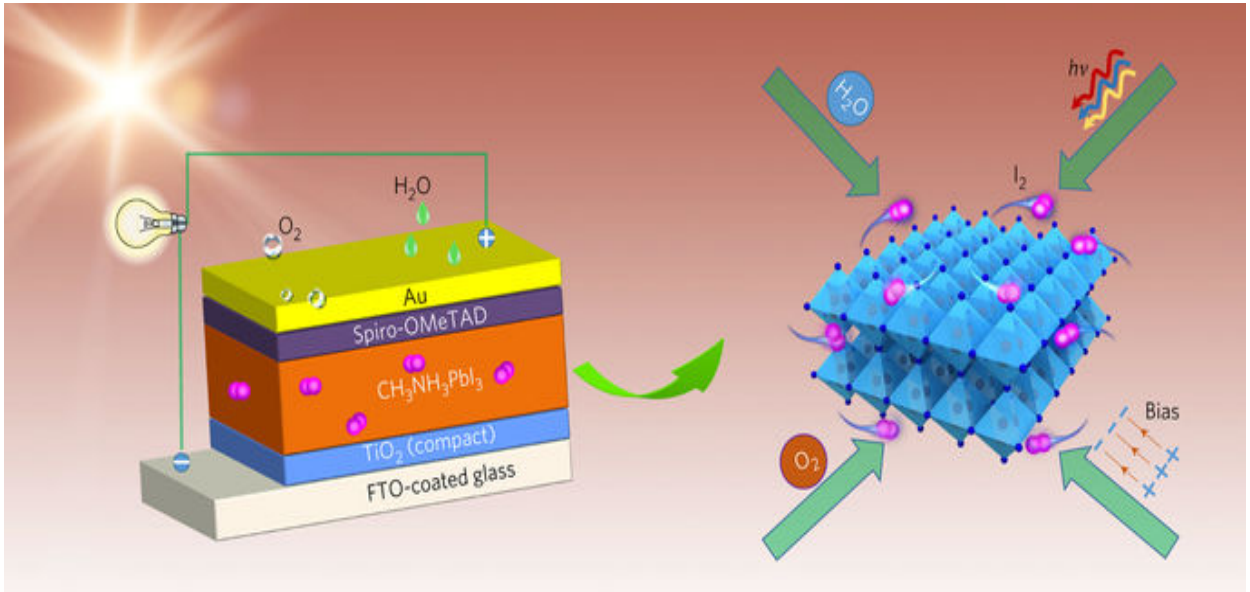
Challenges of perovskite materials:

- Degradation of perovskite materials.
- Lead toxicity concern is also another problem of PSCs.



Introduction

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- With the photovoltaic community aware of the dangers associated with the use of lead in PSCs [13,14], research has been focused on replacing lead in perovskite materials with other non-toxic metals such as Bi, Ge, and Sb [5,6].

- This review is focused on the structural, optical, and stability properties of halide double perovskites and the research progress attained so far towards producing lead-free PSCs.

Heterovalent Substitution

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- Two methods are used:

  1. Substitution of Pb^{2+} with trivalent cations such as Bi^{3+} and Sb^{3+}

  2. Mixed valence approach.

Substitution with a trivalent cation

- Results in $A_3^+B_2^{3+}X_9^-$ perovskite. Park et al. [7] reported a power conversion efficiency (PCE) of about 1% obtained with a PSC employing a hexagonal $Cs_3Bi_2I_9$ perovskite belonging to the $P6_3/mmc$ space group as a light absorber.

- $A_3^+B_2^{3+}X_9^-$ perovskites are characterized by:

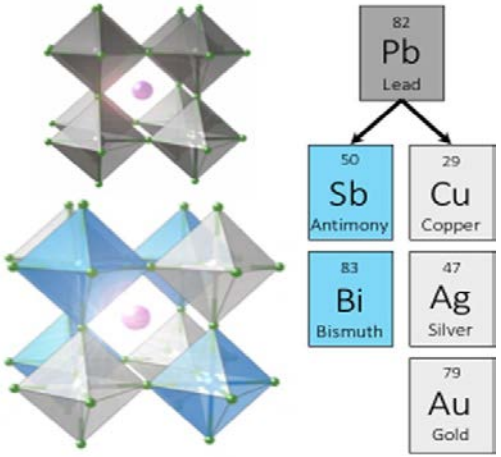
  1. Wide band gaps

  2. Low structural dimensionality

Heterovalent Substitution

Mixed valence approach:

- Substitution of Pb^{2+} with two cations, (1) a monovalent metal cation and (2) a trivalent metal cation resulting in a $A_2B'B''X_6$ double perovskite.



- Most of the investigated halide double perovskites have Sb^{3+} and Bi^{3+} as the replacement for Pb^{2+} [8-10].

Heterovalent Substitution

- There is need to investigate other trivalent cations such as lanthanides, which are thought to have interesting optoelectronic properties [11].

- Lanthanide-based halide double perovskites have been synthesized before [12], although to date there has been no report on their optoelectronic and photovoltaic properties.

Structure

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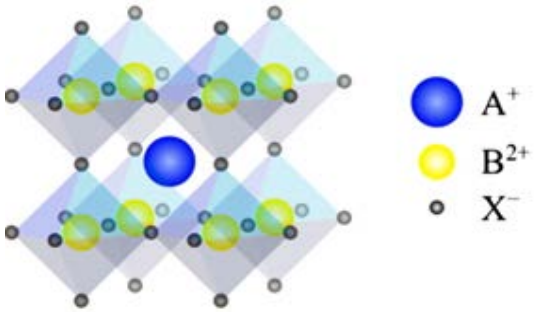
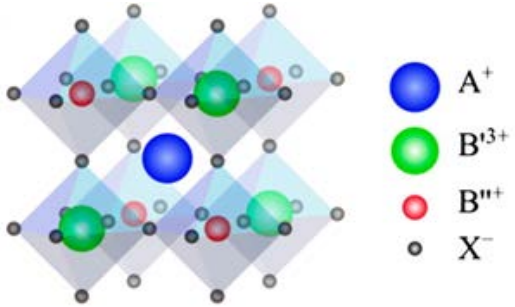
- Cubic face-centered structure belonging to the space group *Fm-3m* and with a lattice parameter ranging from approximately 10–12 Å [13–15].
- 3D framework known as rock salt ordering.
- Volonakis et al. [14] synthesized another lead-free double perovskite of the formula $Cs_2InAgCl_6$ with cubic structure belonging to *Fm-3m* . $Cs_2InAgCl_6$ exhibited a band gap of 3.3 eV.
- Wei et al. [16] synthesized a hybrid double perovskite ($(MA)_2KBiCl_6$) which crystallized in a 3D distorted structure belonging to the *R3-m* space group



Hybrid perovskite.
©RSC2018



Halide double perovskite
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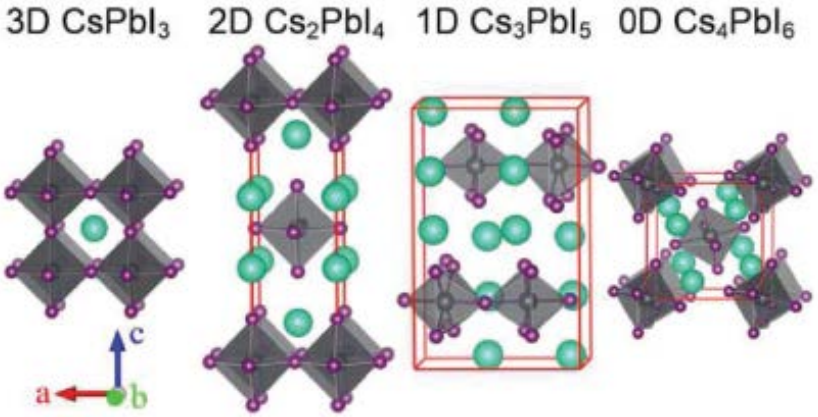
Structure



Lead halide perovskites. © ACS 2016.

- 3D have exhibited better photovoltaic performance.

- . Xiao et al. [17] introduced the concept of electronic dimensionality to help explain why the 3D halide double perovskites do not exhibit ideal photovoltaic performance as their 3D hybrid halide perovskites counterparts do

Optical properties

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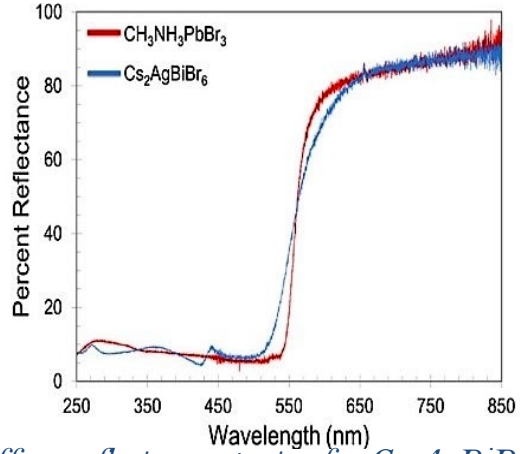
- Halide double perovskites are mostly characterized by indirect and wide bandgaps. UV-Vis diffuse spectra recorded by McClure et al. [10] showed that both $Cs_2AgBiCl_6$ and $Cs_2AgBiBr_6$ exhibited indirect bandgaps.



UV-Vis diffuse reflectance spectra for $Cs_2AgBiBr_6$ and $MAPbBr_3$
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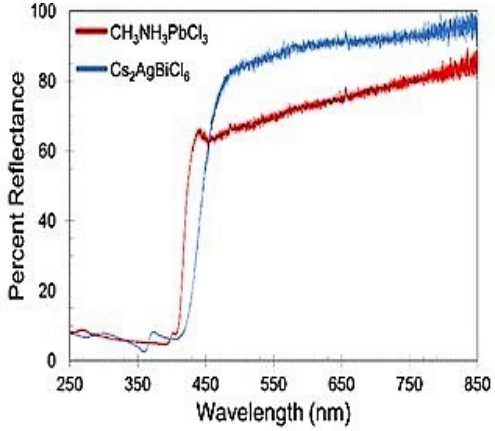
- Optical band gap: 2.77 eV



UV-Vis diffuse reflectance spectra for $Cs_2AgBiCl_6$ and $MAPbBr_3$
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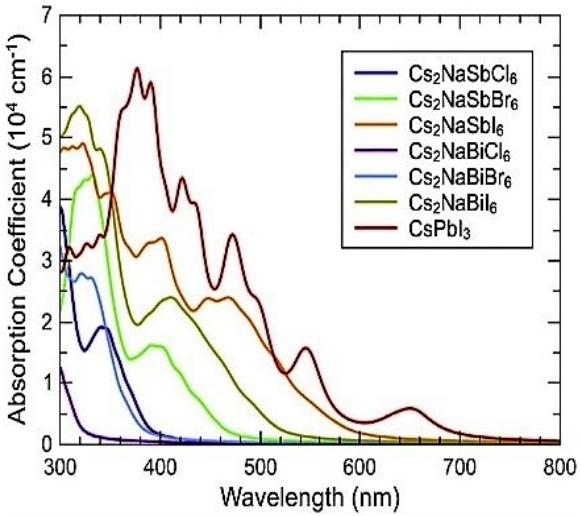
- Optical band gap: 2.19 eV

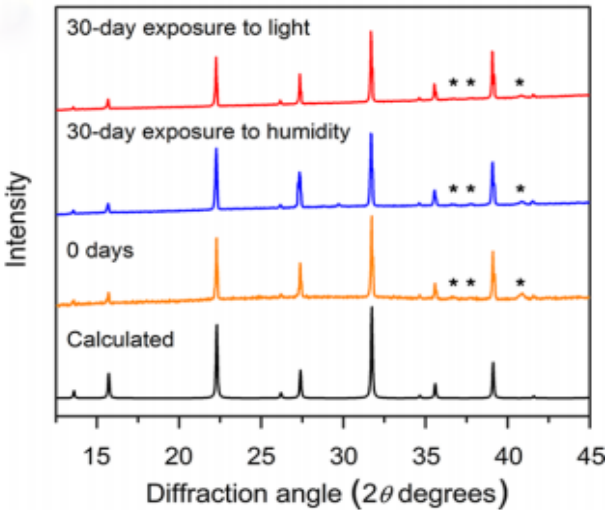
Optical properties



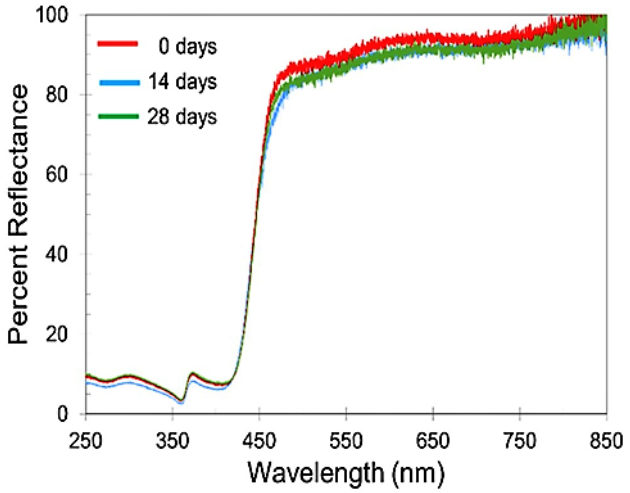
Optical absorption spectra for Cs_2NaBX_6 perovskites. © Elsevier 2017.

- Investigation into the optical characteristics of the sodium-based perovskites Cs_2NaBX_6 (where B = Sb, Bi; X = Cl, Br, I) yielded iodide perovskites Cs_2NaSbI_6 and Cs_2NaBiI_6, with optimal bandgaps of 2.03 eV and 2.43 eV, respectively [13].

Stability



PXRD patterns of $Cs_2AgBiBr_6$ after exposure to humidity (55% RH) or light (0.75 Sun). Asterisks denote signals from the sample holder. © ACS 2016.



UV−vis diffuse reflectance spectra showing the light stability of Cs2AgBiCl6 after 2 and 4 weeks of light exposure. © ACS 2016

- Slavney et al. [18] probed the stability of $Cs_2AgBiBr_6$ when exposed to weather elements.

- McClure et al. [10] probed the stability of $Cs_2AgBiCl_6$ and $Cs_2AgBiBr_6$ in ambient atmosphere.

Stability

The Goldschmidt tolerance factor and octahedral factor

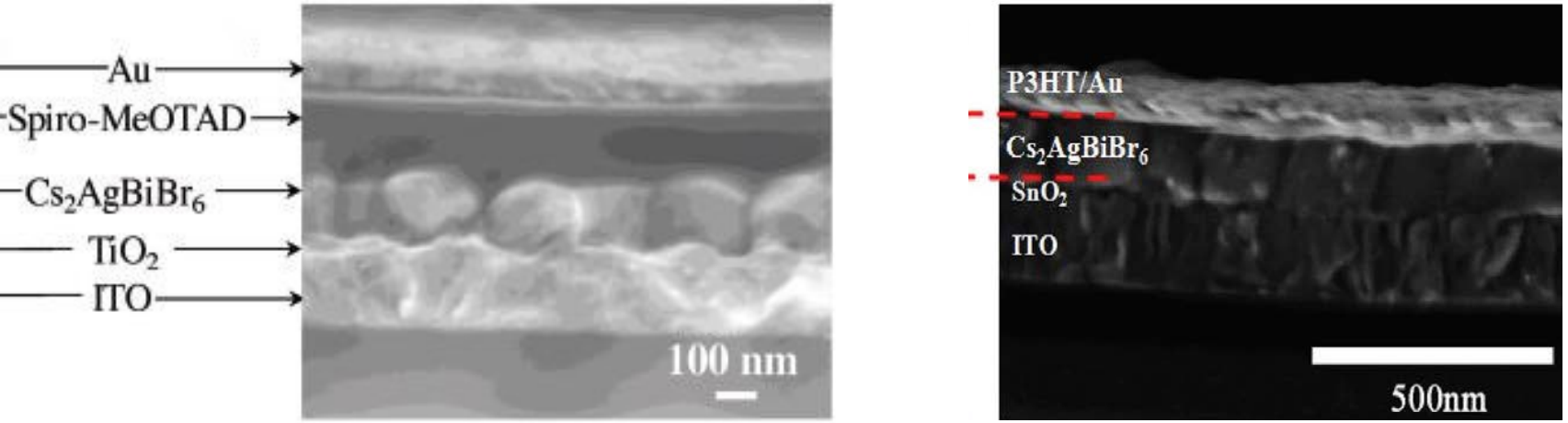
- The Goldschmidt tolerance factor (t) and octahedral factor (μ) are two empirical quantities that are used to evaluate the stability of perovskite crystals.

- The formability of the halide perovskite requires $0.81 < t < 1.11$ while $0.44 < \mu < 0.90$, with t_{eff} and μ_{eff} governed by the following equations [10].

$$t_{eff} = (R_A + R_X)/\{(R_{B'} + R_{B''})/2 + R_X\}$$
$$\mu_{eff} = (R_{B'} + R_{B''})/2R_X$$

- where, R_A, $R_{B'}$, $R_{B''}$ and R_X are Shannon ionic radii of the monovalent cation (e.g. Cs^+), monovalent cation (e.g. Ag^+), trivalent cation and halide anion respectively [9].

Progress of double perovskites



SEM images of (PSCs)-based on $Cs_2AgBiBr_6$ perovskite. © RSC 2017 .

- Ning et al. [19] also a reported a PCE of 1% using a Au/SpiroMeOTAD/$Cs_2AgBiBr_6$/TiO_2/ITO device architecture.

- Wu et al. [20] reported an PCE of 1.44% using a Au/P3HT/$Cs_2AgBiBr_6$/SnO_2/ITO device architecture.

Progress of double perovskites

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- Slavney et al. [21] reported a Tl-doped $Cs_2(Ag_{1-a}Bi_{1-b})Tl_xBr_6$ double perovskite with a bandgap reduced by 0.5 eV at x = 0.075.

- Using $Cs_2AgBiBr_6$ as a host, Du et al. [22] investigated band modification with Sb^{3+} and In^{3+} on the Bi^{3+} lattice site.

- UV-Vis data showed that the bandgap of $Cs_2Ag(Bi_{1-x}In_x)Br_6$ increased from 2.12 to 2.27 eV as x increased to 0.75. However, a decrease of 0.26 eV was noted for $Cs_2Ag(Bi_{1-x}Sb_x)Br_6$ as x increased from 0 to 0.375.

Progress of double perovskites

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- Zhou et al. [24] reported for the first time highly crystalline $Cs_2AgBiBr_6$ nanocrystals fabricated using a hot injection method. The $Cs_2AgBiBr_6$ nanocrystals exhibited impressive photoconversion of CO_2 into solar fuels, with an electron consumption of 105 μmol g^{-1} in 6 h.

- Volonakis et al. [25] investigated the photocatalytic capabilities of $Cs_2AgBiBr_6$, $Cs_2AgBiCl_6$, $Cs_2AgSbBr_6$, and $Cs_2AgInCl_6$ in water splitting. This discovery proves that the application of halide double perovskites can go beyond replacing hybrid lead halide in PSCs.

Table 1. Summary of some of the studied halide double perovskites showing space group, synthesis techniques, and bandgaps.

Perovskite	Space Group	Synthesis Route	Bandgap (Measured/Theoretical eV)	PCE%	References
$Cs_2AgInCl_6$	Fm3m	Solvent evaporation	3.3/2.7 ± 0.6	-	[11]
	Fm3m	Hydrothermal	3.23/3.33	-	[10]
$Cs_2AgBiCl_6$	Fm3m	Solvent evaporation	2.77/2.62	-	[16]
	Fm3m	Solid state	2.2/2.4	-	[14]
	Fm3m	Solid state/solvent evaporation	2.4/-	-	[61]
$^1Cs_2AgBiBr_6$	Fm3m	Solvent evaporation	2.19/2.06	-	[16]
	Fm3m	Solid state	1.9/1.8	-	[14]
	Fm3m	Solid cooling	1.95/-	-	[15]
	Fm3m	Solid state/solvent evaporation	1.8/-	-	[11]
	Fm3m	Hydrothermal	2.05/-	1.22	[11]
	Fm3m	Hydrothermal	-	1.44	[12]
Cs_2AgBiI_6	Fm3m	-	-/1.6	-	[14]
$Cs_2AuBiCl_6$	Fm3m	-	-/1.6	-	[14]
$Cs_2CuBiCl_6$	Fm3m	-	-/2.0	-	[14]
$Cs_2CuBiBr_6$	Fm3m	-	-/1.9	-	[34]
Cs_2CuBiI_6	Fm3m	-	-/1.3	-	[14]
$Cs_2AgInBr_6$	Fm3m	-	-/1.50	-	[13]
$Rb_2AgInCl_6$	Fm3m	-	-/2.5	-	[13]
$Rb_2AgInBr_6$	Fm3m	-	-/1.46	-	[13]
$Rb_2CuInCl_6$	Fm3m	-	-/1.36	-	[13]
$(MA)_2AgBiBr_6$	Fm3m	Hydrothermal	2.0/2.02	-	[9]
$(MA)_2KBiCl_6$	R3m	Hydrothermal	3.04/3.08	-	[8]
$(MA)_2AgSbI_6$	R3m	Solid state	1.93/2.12	-	[10]

Conclusion

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- Most of the studied double perovskites crystallized into 3D structures and exhibited better stability than hybrid lead halide perovskites.

- Most of the reported halide double perovskites have exhibited indirect and wide bandgaps, which are not suitable for solar photovoltaic applications.

- A few of the halide double perovskites such as $Cs_2InAgCl_6$ have direct bandgaps and can be employed in tandem solar cells since they have wide bandgaps.

Conclusion

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- To the best of our knowledge, only $Cs_2AgBiBr_6$ halide double perovskite has been employed as a light absorber in planar heterojunction solar cells, exhibiting PCE of about 1%.

- Considering that most halide double perovskites have wide bandgaps, investigating the performance of these halide double perovskites in tandem solar cells might produce promising results. They can also be explored in photocatalytic application.

- Presently, halide double perovskites might not be adequate replacements for hybrid lead halide perovskites in single junction solar cells.

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