Potential Substitutes for Replacement of Lead in Perovskite Solar Cells: A Review

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Lead halide perovskites have displayed the highest solar power conversion efficiencies of 23% but the toxicity issues of these materials need to be addressed. Lead-free perovskites have emerged as viable candidates for potential use as light harvesters to ensure clean and green photovoltaic technology. The substitution of lead by Sn, Ge, Bi, Sb, Cu and other potential candidates have reported efficiencies of up to 9%, but there is still a dire need to enhance their efficiencies and stability within the air. A comprehensive review is given on potential substitutes for lead-free perovskites and their characteristic features like energy bandgaps and optical absorption as well as photovoltaic parameters like open-circuit voltage ($V_{OC}$), fill factor, short-circuit current density ($J_{SC}$), and the device architecture for their efficient use. Lead-free perovskites do possess a suitable bandgap but have low efficiency. The use of additives has a significant effect on their efficiency and stability. The incorporation of cations like diethylammonium, phenylethyl ammonium, phenylethyl ammonium iodide, etc., or mixed cations at different compositions at the A-site is reported with engineered bandgaps having significant efficiency and stability. Recent work on the advancement of lead-free perovskites is also reviewed.

1. Introduction

Perovskite originally referred to a mineral calcium titanium oxide, CaTiO$_3$, discovered in 1839 in Ural Mountains of Russia by Gustav Rose, a German mineralogist and later named after a Russian mineralogist count Lev Aleksevich Perovski.$^{[1]}$ Since then, the term perovskite has been used for any organic/inorganic compound (synthetic/natural) with the similar crystal structure and stoichiometry as of CaTiO$_3$, that is, ABX$_3$, where A is monovalent metallic cation, most usually from group I of the periodic table. B is divalent metallic cation, a transition metal and X is a nonmetallic anion (halide). However, for O$_2^-$ anions, A and B are divalent and tetravalent cations, respectively. The size of cation A must be larger than that of cation B. Ideally, perovskite crystal structure is described as a body centered cubic structure with monovalent cation A 12-fold coordinated by X anions as shown in Figure 1.$^{[2]}$ The volume occupied by A ions depends on the electronegativity and size of B and X ions, respectively. A superfluity of organic/inorganic compounds has been discovered that exists in perovskite crystal structure framework ABX$_3$ like BaTiO$_3$, SrTiO$_3$, KNbO$_3$, etc.

Generally, perovskite materials can be classified into two groups, namely, inorganic oxide perovskite and halide perovskite that further encompass alkali halide and organometal halide perovskite materials. There are some perovskite materials like MgCNi$_3$ having neither oxygen nor halide component and...
hence do not belong to either of the groups.\textsuperscript{[3]} In alkali halide perovskites, A-site is occupied by a monovalent organic cation such as CH\textsubscript{3}NH\textsubscript{3} (methylammonium or MA), NH\textsubscript{2}(CH)NH\textsubscript{2} (formamidinium or FA), or inorganic cations such as rubidium (Rb), caesium (Cs), etc., the B-site by a divalent metal cation lead (Pb) or tin (Sn), and X-site by a halide anion. In today’s scientific world, it is the halide perovskites that have grabbed all the attention of silicon-dominated photovoltaics industry and whole of the photovoltaics research is now focused in developing perovskite materials for solar energy conversion.

The suitability of a particular combination of cations to organize into a perovskite structure can be estimated based on two important parameters. The first one is the Goldschmidt tolerance factor (\( t \)), a dimensionless number, calculated from the ratio of ionic radii\textsuperscript{[4]}

\[
t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}
\]

where \( r_A \) and \( r_B \) are the ionic radii of cations A and B, and \( r_X \) is the ionic radius of anion. For a particular perovskite structure, the tolerance factor (\( t \)) can be calculated by substituting the ionic radii of cations and anions. If \( t = 1 \), it indicates the formation of an ideal cubic structure having size of cation A larger than that of B. The tolerance factor (\( t \)) must lie in the range of 0.8–1.0 for the formation of stable perovskite structures. If \( t < 0.8 \) or \( t > 1.0 \), the cation A is too small or too big to fit into BX\textsubscript{6} octahedron, thereby resulting in the formation of alternative structures. The tolerance factor (\( t \)) leading to formation of different types of structures with examples is mentioned in Table 1.

The second one is the octahedral factor (\( \mu \)) which is the ratio between ionic radii of B and X

\[
\mu = \frac{r_B}{r_X}
\]

The octahedral factor (\( \mu \)) must lie in the range of 0.44–0.72 for B and X in order to form a stable BX\textsubscript{6} octahedron.\textsuperscript{[2]} The tolerance factor has an immense role to play in finding alternative lead halide perovskite materials as many different cations can be inserted in ABX\textsubscript{3} structure framework leading to development of varied materials with specific engineered properties.\textsuperscript{[8]}

The effective ionic radii of organic molecular cations and Shannon ionic radii of inorganic cations as well as the effective ionic radii of various anions are listed in Table 2.\textsuperscript{[9–13]}

The Goldschmidt tolerance factor (\( t \)) has played a pivotal role in development of perovskites\textsuperscript{[10]} and is now being used to engineer/synthesize new organic–inorganic stable perovskites structures by formulating the composition of perovskite. The tolerance factor can be tuned to the stable perovskite range by mixing distinct A/B cations and X anions in a particular composition.\textsuperscript{[14–17]}

### 2. Perovskite Sensitized Solar Cell

Solar energy has always been sought to be converted into electrical energy through photovoltaic effect of light absorbing semiconductor in order to obtain clean and green energy. The traditional first generation crystalline silicon solar employed for this purpose enjoy a market share of more than 90% in PV market.\textsuperscript{[18]} The second generation solar cells consist of thin films such as cadmium telluride, copper indium gallium selenide, and amorphous silicon. The third generation has a number of thin film technologies such as dye-sensitized solar cells (DSSCs) in development phase. The crystalline silicon solar cell has a theoretical limiting power efficiency of 33.16%\textsuperscript{[19]} noted as a Shockley Queisser limit in 1961. An efficiency of 25.6%\textsuperscript{[20]} for a silicon solar cell has been reported in 2014 that further grows to 46.1%\textsuperscript{[21]} in four-junction GaInP/GaAs/GaInAs/GaInAs solar cell reported by French-German collaboration. The triple-junction thin film solar cells achieved an efficiency of 13.6% in June 2015,\textsuperscript{[22]} The research teams at NREL, EPFL, and GSEM have reported Sun efficiencies of dual-junction GaInP/GaAs solar cell devices up to 32.8%.\textsuperscript{[23]} Although, the monocrystalline silicon cells have photovoltaic conversion efficiency of more than 20%,\textsuperscript{[24]} they are characterized by high cost, difficult preparation conditions, and serious environmental pollution.\textsuperscript{[25]}

### Table 1. Goldschmidt tolerance factor (\( t \)) of various perovskite materials.\textsuperscript{[5]}

| Goldschmidt tolerance factor (\( t \)) | Structure | Example |
|--------------------------------------|-----------|---------|
| 0.9–1.0                              | Cubic     | SrTiO\textsubscript{3}\textsuperscript{[6]} BaTiO\textsubscript{3}\textsuperscript{[27]} |
| 0.71–0.9                             | Several perovskite structures/orthorhombic rhombohedral | GdFeO\textsubscript{3}, CaTiO\textsubscript{3}\textsuperscript{[6]} |
| <0.71                                | Ilmenite  | FeTiO\textsubscript{3}, KNbO\textsubscript{3}\textsuperscript{[1]} |
| >1                                   | Hexagonal or tetragonal | BaNiO\textsubscript{2}\textsuperscript{[6]} |
thin film solar cells’ large-scale use puts a pressure on environmental pollution. DSSCs showing an efficiency of more than 13% have low cost and easy fabrication but absorption layer in such cells is very thick\cite{26} and light dyes used in such cells suffer from phenomenon of light bleaching.

An efficient solar cell technology must ensure low raw material and finished material cost, high light absorption and solar power conversion efficiency, high abundance of raw material, low toxicity, and less environmental pollution. In order to achieve it, the organic/inorganic perovskite compounds can be used in light harvesting layer as these materials have all the requisite properties that make them suitable for use in PV\cite{27} applications. With the discovery of metal halide perovskite, especially MAPbI$_3$, FAPbI$_3$ as light absorbers, the use of perovskites

| Cation A | Effective ionic radii ($r_{\text{eff}}$) [pm] | Ref. |
|-----------------|---------------------|-----|
| Ammonium [NH$_4$]$^+$ | 146 | [10] |
| Hydrazinium [NH$_3$NH$_2$]$^+$ | 217 | [10] |
| Azetidinium [CH$_2$NH$_2$]$^+$ | 250 | [10] |
| Formamidinium [CH(NH$_2$)$_2$]$^+$ | 253 | [10] |
| Imidazolium [C$_3$N$_2$H$_7$]$^+$ | 258 | [10] |
| Dimethylammonium [CH$_2$NH$_2$]$^+$ | 272 | [10] |
| Ethyl ammonium [CH$_2$CH$_2$NH$_2$]$^+$ | 274 | [10] |
| Guanidinium [(NH$_2$)$_2$C]$^+$ | 278 | [10] |
| Tetramethylammonium [CH(NH$_2$)$_2$]$^+$ | 292 | [10] |
| Thiazolium [C$_3$H$_4$NS]$^+$ | 320 | [11] |
| Tropylium [C$_3$H$_5$]$^+$ | 333 | [11] |
| Hydroxylamine [NH$_2$OH]$^+$ | 216 | [10] |
| Methylammonium [CH$_2$NH$_2$]$^+$ | 217 | [10] |
| Piperazinium [C$_4$H$_8$N$_2$]$^+$ | 322 | [9] |
| Dabconium [C$_4$H$_8$N$_2$]$^+$ | 339 | [9] |
| K$^+$ | 164 | [12] |
| Rb$^+$ | 172 | [12] |
| Cs$^+$ | 188 | [12] |
| Pb$^{2+}$ | 119 | [12] |
| Eu$^{2+}$ | 117 | [12] |
| Tm$^{3+}$ | 103 | [12] |
| Yb$^{3+}$ | 103 | [12] |
| Sn$^{4+}$ | 69 | [12] |
| Te$^-$ | 150 | [12] |
| Au$^+$ | 137 | [12] |
| Au$^{3+}$ | 85 | [12] |
| Sb$^+$ | 76 | [12] |
| Bi$^{3+}$ | 103 | [12] |
| Te$^{4+}$ | 97 | [12] |
| La$^{3+}$ | 103 | [12] |
| Ce$^{3+}$ | 101 | [12] |
| Pr$^{3+}$ | 99 | [12] |
| Nd$^{3+}$ | 98 | [12] |
| Sm$^{3+}$ | 96 | [12] |
| Eu$^{3+}$ | 95 | [12] |
| Gd$^{3+}$ | 94 | [12] |
| Dy$^{3+}$ | 91 | [12] |
| Er$^{3+}$ | 89 | [12] |
| Tm$^{3+}$ | 88 | [12] |
| Lu$^{3+}$ | 86 | [12] |
| Pd$^{2+}$ | 100 | [12] |
| Am$^{3+}$ | 98 | [12] |
| Bk$^{3+}$ | 96 | [12] |

| Anion X | Effective ionic radii ($r_{\text{eff}}$) [pm] | Ref. |
|-----------------|---------------------|-----|
| Fluoride, F$^-$ | 129 | [9] |
| Chloride, CF$^-$ | 181 | [9] |
| Bromide, Br$^-$ | 196 | [9] |
| Iodide, I$^-$ | 220 | [10] |
| Formate, HCOO$^-$ | 136 | [9] |
| BH$_4^-$ | 203 | [11] |

| Cation B | Effective ionic radii ($r_{\text{eff}}$) [pm] | Ref. |
|-----------------|---------------------|-----|
| Be$^{2+}$ | 16 | [12] |
| Mg$^{2+}$ | 72 | [12] |
| Ca$^{2+}$ | 100 | [12] |
| Sr$^{2+}$ | 118 | [12] |
| Ba$^{2+}$ | 135 | [12] |
| Mn$^{2+}$ | 66 | [12] |
| Fe$^{2+}$ | 84 | [12] |
| Co$^{2+}$ | 58 | [12] |
| Ni$^{2+}$ | 55 | [12] |
| Pd$^{2+}$ | 86 | [12] |
| Pt$^{2+}$ | 60 | [12] |
| Cu$^{2+}$ | 73 | [12] |
| Zn$^{2+}$ | 60 | [12] |
| Cd$^{2+}$ | 78 | [12] |
| Hg$^{2+}$ | 69 | [12] |
| Ge$^{4+}$ | 73 | [12] |
| Sn$^{4+}$ | 110 | [13] |
in PV technology has been explored as they are cost effective and readily available for large-scale use. \cite{32,32,34,35,36,37,38,39} The organic–inorganic perovskite materials have been pioneering in fabricating high solar power conversion efficiency hybrid solar cells from time to time. \cite{40,41,42,43,44,45} Miyasaka and co-workers reported the first perovskite sensitized solar cell (PSSC) in 2006 and 2008 using CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ absorbers and reported solar power conversion efficiency varying between 0.4 and 2% for solid-state and liquid electrolyte cells, respectively. \cite{46,47} A MAPbI$_3$-based solar cell with solar power conversion efficiency of 3.8% has been reported by Kojima et al. in 2009 and was the first peer reviewed publication on perovskite-sensitized solar cell. \cite{48} Park and co-workers using CH$_3$NH$_3$PbI$_3$ liquid electrolyte solar cell reported an improved efficiency of 6.5%. \cite{49} In 2011, Snaith along with his co-workers developed a solid-state perovskite solar cell (PSC) using 2,2(7,7)-tetrakis-(N,N-dimethoxyphenylamine)9,9(Spiro-bifluorene) (Spiro-OMeTAD) for hole transportation and produced solar power conversion efficiencies between 8 and 10%\cite{50} achieving a major breakthrough in performance efficiency of PSSC in comparison to DSSCs having only 7% efficiency. \cite{51} In 2012, Kim et al. replaced the liquid electrolyte with a solid-state hole conducting material depositing the perovskite precursor over the mesoporous TiO$_2$ layer achieving a solar power conversion efficiency (SPCE) of 9.7%. \cite{52} Later, increased efficiencies of 10.9% were reported by Lee et al.\cite{53} Gratzel and co-workers reported a SPCE of 15% by using sequential deposition to produce pinhole-free perovskite layer. \cite{54} Liu et al. Introduced Zn$_2$SnO$_4$ nanocrystalline thin film on PCBM buffer layer to make electron extraction process easy, thereby, increasing SPCE to 17.7%.\cite{55} You et al. and Yang et al. first fabricated all metal oxide layer based perovskite solar cell reporting an efficiency of 16.1% and more stability of the material in 2016.\cite{56} Yang et al. and his team reported SPCE of 22.1%\cite{57} in defect engineered thin perovskite layers in PSSCs containing formamidinium with multiple cations and mixed halide anions in 2017. The SPCE of solid-state PSSCs was around 10% in 2012 that later grew up to 22.1% in 2017. This has been achieved through engineering of perovskite composition and thin film deposition methods. The big issue of degradation of perovskite in polar liquid electrolyte has been solved by use of solid-state PSCs that have shown 500 h stability in ambient conditions without encapsulation but still the PSSCs have to prove its stability in air, on exposure to humidity,\cite{58,59,60,61} UV light,\cite{62} and high temperatures.\cite{63,64} Research has also revealed that PSSCs also suffer from anomalous current–voltage hysteresis as reported by Snaith and co-workers in 2014\cite{65} that can have adverse effects on the stability of PSSCs.\cite{66,67}

### 3. Device Configuration and Working Principles of Perovskite Solar Cell

In the first perovskite solar cell fabricated in 2009, perovskite nanoparticles were used as a light absorber replacing dyes in dye-sensitized solar cells. In the fabricated device, mesoporous TiO$_2$ layer of several micrometer thickness acts as an anode and a platinum-coated glass acted as a cathode in a liquid electrolyte based device.\cite{28,29} However, the device suffered seriously from the stability issue as the perovskite light absorber layer dissolves or decomposes in the liquid electrolyte very rapidly. Hence, the liquid electrolyte was replaced by a solid-state material to act as a hole transport material (HTM) resulting in a solid-state mesoscopic perovskite solar cell with an improved stability. Organic Spiro-OMeTAD was used as a hole transport material in such cells.\cite{68} The perovskite materials when used as a light absorber enhances the device stability and performance to its broad optical absorption range than the conventional dyes.\cite{69}

In a mesoscopic perovskite solar cells, a compact metal oxide (TiO$_2$) layer is deposited on a fluorine-doped tin oxide (FTO) glass substrate by spin-coating on which is further deposited mesoporous TiO$_2$ layer by spin-coating. The perovskite light absorber layer is grown on the scaffold of mesoporous TiO$_2$ layer which is further deposited by a HTM by spin-coating and finally to a metal-back electrode (Ag or Au). The device configuration of mesoporous perovskite solar cell is shown in Figure 2a.\cite{70} TiO$_2$ is most commonly employed in mesoporous layer that facilitates in the formation of inner connected layer of perovskite crystals by allowing their deep penetration into the pores of mesoporous layer. Compact TiO$_2$ layer transports electrons, blocks holes, and suppresses the recombination of electron–hole pairs. The mesoporous TiO$_2$ layer needs a high-temperature sintering that can consequently increase the device fabrication time. Since the perovskite materials have ambipolar nature, they have the potential of transporting electrons and holes on their own in between two electrodes so a planar structure is viable for them.\cite{71} Also, the perovskite solar cells

![Figure 2](image.png)

Figure 2. a) Device structure of mesoporous PSCs, b) planar heterojunction, c) inverted planar PCSs, and d) HTM-free PSCs. Reproduced with permission.\cite{66} Copyright 2016, Springer Nature.
using planar structure over time have revealed the best device performance as that of a mesoporous structure.\textsuperscript{[32,67]} The device with planar configuration has reported almost 100% internal quantum efficiencies ascertaining them as an efficient device structure.\textsuperscript{[63]} Thus, typically there are two major device configurations for a perovskite solar cell, viz., a planar heterojunction/conventional structure (n-i-p) and an inverted planar structure (p-i-n). In a planar heterojunction structure (n-i-p) as shown in Figure 2b,\textsuperscript{[66]} a compact electron transport layer (ETL) of TiO\textsubscript{2} of 30–50 nm of TiO\textsubscript{2} (most commonly) is deposited on a transparent conducting oxide substrate that can be indium-doped tin oxide (ITO) or FTO. The mesoporous TiO\textsubscript{2} layer is removed and perovskite light absorber to sandwich between an ETL and a hole transport layer (HTL) by spin-coating or by vapor deposition and vapor-assisted solution process on a compact TiO\textsubscript{2}\textsuperscript{[32,33]} layer and finally connected to a metal electrode such as Au, Ag, or Pt. Spiro-OMeTAD or poly-triaryllamine (PTAA) can be used in ETL. For an inverted planar structure (p-i-n) as shown in Figure 2c,\textsuperscript{[66]} a hole transport layer (HTL) by spin-coating or by vapor deposition to a metal electrode such as Au, Ag, or Pt. Spiro-OMeTAD or poly-triaryllamine (PTAA) can be used in ETL. For an inverted planar structure (p-i-n) as shown in Figure 2c,\textsuperscript{[66]} a hole transport layer (HTL) by spin-coating or by vapor deposition and vapor-assisted solution process on a compact TiO\textsubscript{2}\textsuperscript{[32,33]} layer and finally connected to a metal electrode such as Au, Ag, or Pt. Spiro-OMeTAD or poly-triaryllamine (PTAA) can be used in ETL. For an inverted planar structure (p-i-n) as shown in Figure 2c,\textsuperscript{[66]} a hole transport layer (HTL) by spin-coating or by vapor deposition and vapor-assisted solution process on a compact TiO\textsubscript{2}\textsuperscript{[32,33]} layer and finally connected to a metal electrode such as Au, Ag, or Pt. Spiro-OMeTAD or poly-triaryllamine (PTAA) can be used in ETL. For an inverted planar structure (p-i-n) as shown in Figure 2c,\textsuperscript{[66]} a hole transport layer (HTL) by spin-coating or by vapor deposition and vapor-assisted solution process on a compact TiO\textsubscript{2}\textsuperscript{[32,33]} layer and finally connected to a metal electrode such as Au, Ag, or Pt. Spiro-OMeTAD or poly-triaryllamine (PTAA) can be used in ETL. For an inverted planar structure (p-i-n) as shown in Figure 2c,\textsuperscript{[66]} a hole transport layer (HTL) by spin-coating or by vapor deposition and vapor-assisted solution process on a compact TiO\textsubscript{2}\textsuperscript{[32,33]} layer and finally connected to a metal electrode such as Au, Ag, or Pt. Spiro-OMeTAD or poly-triaryllamine (PTAA) can be used in ETL.

### 4. Why Lead-Free?

The use of organic–inorganic lead halide perovskite such as MAPb\textsubscript{I}\textsubscript{3} and FAPb\textsubscript{I}\textsubscript{3} has caused an increase in solar power conversion efficiencies from 3.8% in 2009\textsuperscript{[28]} to 22.1%\textsuperscript{[14,35,73–76]} in last nine years as these materials do possess requisite opto-electronic features such as a direct band gap, long charge carrier lifetime, diffusion length, high charge carrier mobility, and strong optical absorption coefficient.\textsuperscript{[77–90]} Lead halide perovskite has high open-circuit voltages due to photon recycling as a result of which they have long charge extraction lengths through multiple absorption–emission events within the perovskite active layer.\textsuperscript{[91]} The metal lead has invaluable intrinsic properties like high melting point, high density, malleability, ductility, corrosion resistance, etc. Despite having all characteristic features to be exploited in commercial PV solar market, it is the toxic nature of lead in halide perovskite solar cells that hinders its use in silicon-dominated PV market. The stringent directives of European Union clearly prohibits the use of hazardous substance in electrical and electronic equipment and lead has been identified as one of the ten hazardous chemicals listed by ROHS in order to avoid its exposure to person and people as well.\textsuperscript{[92,93]} The toxicity of lead is due to its affinity for band formation with thiol and cellular phosphate groups of numerous enzymes, proteins, and cell membranes.\textsuperscript{[94]} Lead halide perovskite solar cells do contain a considerable portion of lead, that is, 33% by weight. Lead is carcinogenic in nature and has no safe threshold limit of exposure. It can cause serious toxicological implications on human beings leading to cardiovascular and development diseases by inflicting the functioning of liver, kidney, brain, and central nervous system. Exposure to lead can produce irreversible health damages in infants and pregnant ladies.\textsuperscript{[95–97]} Also, organic–inorganic lead halide perovskites are liable to degradation under moisture, rain, heat, and prolonged illumination in air.\textsuperscript{[98–100]} Therefore, instability is another prime issue linked with these materials that reduces their working life span which is the most important prerequisite for commercialization on large scale as PV panels are generally placed over roof tops or in open fields so their exposure to rain is inevitable.

Hailegnaw et al. have reported that in case of a catastrophic failure of a solar panel, the impact of rain of different pHs on MAPb\textsubscript{I}\textsubscript{3} films is complete degradation of perovskite material leaving behind Pb\textsubscript{I}\textsubscript{2} in water in the order of 10\textsuperscript{−8} mol L\textsuperscript{−1} which is of course low but higher than that of CdTe, CdS, and PbS values varying from 10\textsuperscript{−2} to 10\textsuperscript{−34} so it becomes most probable that lead, being soluble in water, may leech into the underground water resources.\textsuperscript{[101]} Not only this, Hailegnaw et al. have analyzed the impact of leaching lead out of the damaged solar panels on the soil and reported that the leakage of lead due to broken encapsulation or sealing will induce the concentration of Pb in first cm of ground below the damaged solar panel by 70 ppm.\textsuperscript{[101]} Taking into consideration the repercussions of use of toxic lead halide perovskites, it becomes pertinent to investigate lead-free perovskite materials providing better stabilities with solar power conversion efficiencies without compromising human health and environment.
5. Characteristic Features of Lead-Free Perovskites

The perovskite based materials used in solar cells do possess such a structure that enables them to have most suitable optical bandgaps to act as a light absorber. These materials do possess a high dielectric constant, long diffusion length, and a broad optical absorption range covering the entire visible spectrum and into the infrared. Perovskite materials exhibit ambipolar properties that enable them to display both n-type and p-type behavior on exposure to photons of incident light. The rate of nonradiative recombination in such material is strongly suppressed that is essential for high solar power conversion efficiencies. The presence of hysteresis loss in these materials clearly indicates the presence of magnetic properties at room temperature or above. Another important characteristic of these materials is that they are deposited by low-temperature solution methods that provide easy fabrication with low production cost. Besides they are typically flexible, light weight, and semitransparent making them more appealing for use in photovoltaic applications.

The lead-based halide perovskites have reported a highest solar power conversion efficiency of 22% up to now within 8 years of research. The efficiency limit of perovskite solar cell has been envisaged to be 31% based on detailed balance calculations much closer to the Shockley–Queisser limit of 33%. Although the lead-based halide perovskites have all the structural, optical, and electrical features for use in perovskite solar cell as a light absorber but due to toxicity issues of lead, it is pertinent to replace it by another suitable elements such as tin, germanium, bismuth, etc. The lead-free perovskites have attracted the attention of the researchers at present time due to significant properties of these materials that can be engineered to make them suitable for their use as light absorbers in perovskite solar cells. Lead-free perovskite methylammonium tin iodide MASnI3 is a direct gap semiconductor with an optical bandgap of 1.3 eV which is close to 1.5 eV of MAPbI3. It exhibits a strong photoluminescence emission corresponding to the onset at 950 nm in 700–1000 nm range of the absorption edge at room temperature. MASnI3 has an electrical conductivity of $5 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature that corresponds to a Seebeck coefficient of $\approx -60 \mu \text{V K}^{-1}$. The material exhibits a carrier concentration of the order of $1 \times 10^{14} \text{ cm}^{-3}$.

Table 3 summarizes the electron and hole mobilities of all the lead-free perovskite materials. The Hall measurements of as-grown crystals of MASnI3 have revealed a hole concentration of about $9 \times 10^{17} \text{ cm}^{-3}$ with a hole mobility of about 200 cm$^2$ V$^{-1}$ s$^{-1}$. Table 3 summarizes the electron and hole mobilities of all the lead-free perovskite materials. The Hall measurements of as-grown crystals of MASnI3 have revealed a hole concentration of about $9 \times 10^{17} \text{ cm}^{-3}$ with a hole mobility of about 200 cm$^2$ V$^{-1}$ s$^{-1}$ at 250 K.
Although tin halide perovskite has higher charge carrier mobilities, Sn$^{2+}$ has a strong tendency to get oxidized to Sn$^{4+}$ causing a p-type self-doping. The artificial hole doping of the halide-based perovskites increases their electrical conductivity and they exhibit a metal-like conducting behavior. The formamidinium tin iodide (FASnI$_3$) has an optical bandgap of 1.41 eV that is much closer to the bandgap 1.5 eV of MAPbI$_3$, making it a potential candidate to display an optical absorption up to 950 nm. The cesium tin iodide (CsSnI$_3$) displays lower light absorption onset at 450 nm with absorption coefficient of $\approx 1 \times 10^5$ cm$^{-1}$ that are lower as compared to MAPbI$_3$ that has an absorption coefficient of around $2 \times 10^5$ cm$^{-1}$ at 450 nm.

Lead-free perovskites have high exciton binding energies that provide them stable optical properties. The exciton binding energies of bismuth-based halide perovskites MA$\text{Bi}_3$I$_9$, Cs$_2$Bi$_4$I$_8$, and MA$_2$Bi$_4$I$_6$Cl$_x$ are of 70, 270, and 300 meV that are much higher than that of lead-based halide perovskites (25–50 meV). UV–vis absorption measurements for Cs$_2$Bi$_4$I$_8$ have reported a strong exciton absorption peak at room temperature. Cs$_2$Bi$_4$I$_8$ exhibits an exciton absorption peak at $\approx 485$ nm (2.56 eV) with an indirect optical bandgap of $\approx 2.1$ eV. The films exhibited an optical absorption coefficient of $\approx 1 \times 10^4$ cm$^{-1}$ at 450 nm. In spite of indirect bandgaps, the material is still a potential candidate for use as a light absorber due to strong exciton binding energy. CsSnI$_3$ perovskite exhibits a direct bandgap of 1.32 eV with an exciton binding energy of 18 meV at room temperature. The large binding energy is on the account of exciton motion in the 2D layer of Sn$I_4$ tetragons present in the material.

Tin-based perovskites are prepared by using solution methods and crystallizes at room temperature whereas lead-based halide perovskites crystallize by heating. The variation in composition of halide anion in lead-free perovskites has a significant effect on the absorption coefficient of these materials thus paving the way for engineering the bandgaps and optical absorption spectrum of these materials. The tin-based hybrid halide perovskites $\text{MAn}_3\text{Bi}_2\text{I}_{x}$Br$_{(3,0,1,2,3)}$ synthesized in an inert atmosphere in the nitrogen glove box exhibit an optical absorption onset that can be blueshifted from 954 to 577 nm by varying the composition of halide anion, that is, for $x = 0$ and $x = 3$ whereas for $x = 1$ and 2, optical absorption onset at 795 and 708 nm has been reported. Also ultraviolet photoelectron spectroscopy (UPS) measurements of valence band energy $E_{VB}$ of $\text{MASnI}_3\text{Br}_x$ under high vacuum have revealed that the bandgaps can be engineered from 1.30 eV for $\text{MASnI}_3$ to 2.15 eV for $\text{MASnBr}_3$. Not only this, the color of the tin-based hybrid halide perovskite $\text{MASnI}_3\text{Br}_x$ shows a variation with increased bromine content from black ($x = 0$) to dark brown ($x = 1$) and yellow ($x = 3$); thus, colorful solar devices can be designed by using bandgap engineering. Thus, the composition of tin-based mixed halide perovskite can be tailored to emit between 954 and 574 nm in contrast to lead-based counterparts that display photovoltaic emission in between 700 and 800 nm. The emitted wavelengths are in agreement with the values of bandgaps obtained through experiments clearly indicating the presence of direct optical bandgaps in $\text{MASnI}_3$.

The investigation of Ge mixed halide perovskites $\text{MAGeI}_{3-x}\text{Cl}_x$ has been reported to have a linear bandgap of 1.8 eV for $\text{MAGeI}_3$ whereas $\text{MAGeCl}_3$ has a much wider bandgap of 3.8 eV clearly demonstrating the effect of doped chlorine in $\text{MAGeI}_3$ perovskites. The absorption coefficients also display an increasing trend when the proportion of $x$ decreases from 3 to 0 attributed to the redshift of the optical bandgap caused due to change in chemical composition of the material. In case of antimony-based mixed halide perovskites $\text{MASbI}_3\text{Br}_{9-x}$, the optical bandgap onset for perovskite films shows a decreasing trend, that is, the optical absorption onset is blueshifted from 558 to 453 nm as $x$ changes from 9 to 0. The hole and electron mobilities of $\text{MASbI}_3$ single crystals have been calculated by using space charge limited current methods and are shown in Table 3. $\text{MA}_{3}\text{Bi}_2\text{I}_9$ single crystals have high absorption coefficient greater than $10^5$ cm$^{-1}$ at absorption peak wavelengths. The absorption onset for $x = 0, 3, 6$ in $\text{MA}_{3}\text{Sb}_{1-x}\text{I}_9\text{Br}_x$ films are 453, 486, and 516 nm with a direct bandgap of 2.78, 2.66, and 2.49 eV, respectively.

Lead-free perovskites do possess suitable carrier diffusion lengths and minority charge carrier lifetimes exhibiting photovoltaic performance. The long carrier diffusion lengths of electrons and holes in $\text{MASnI}_3$ are 279 ± 88 and 193 ± 46 nm, respectively, obtained by broadband transient absorption and time-resolved fluorescence spectroscopy. Addition of SnF$_2$ in $\text{MASnI}_3$ films results in not only increase in diffusion lengths to more than 500 µm but also enhances the fluorescence lifetime up to ten times. The background concentration of doped holes has an effect on the diffusion lengths of $\text{MASnI}_3$ perovskite. As the background doping level in $\text{MASnI}_3$ decreases, there is a corresponding increase in diffusion length. For a doping concentration below $10^{15}$ cm$^{-3}$, the diffusion length can be engineered to increase above 1 µm in length that is close to the value shown by lead-based halides. Lead-free $\text{CsSnI}_3$ perovskite films synthesized by the solution method have carrier lifetime of $\approx 54$ ps, minority carrier diffusion length of $\approx 1.6$ nm, and a doping concentration of more than $9.2 \times 10^{18}$ cm$^{-3}$ obtained as a consequence of better quality of crystalline films whereas single crystals of $\text{CsSnI}_3$ have a long minority carrier diffusion length of more than 930 nm which is comparable to that of the lead-based perovskites having diffusion lengths exceeding 1 µm.

6. Hole Transport Material and Electron Transport Material in Lead-Free Perovskite Solar Cells

Lead-free perovskites have been prepared by using mesoporous perovskite solar cells in planar heterojunction and inverted planar structures. Spiro-OMeTAD is most commonly used hole transport material in lead-free perovskites as it has the ability to penetrate deep into the pores of the perovskite layer but it has a low hole mobility and complicated device processing. Also it deteriorates the stability of the fabricated device. Therefore, dopants are added into it in order to enhance its conductivity. The first lead-free perovskite device was prepared by solvent engineering method by employing $\text{MASnI}_3$ as a light absorber. Spiro-OMeTAD has been used as
a HTM on the top of the perovskite layer in a device architecture of FTO/compact TiO₂/mesoporous TiO₂ layer/MASnI₃ light absorber/Spiro-OMeTAD/Au. An additive doping of hydrogen bis(trifluoromethane sulfonylimide) (H-TFSI) and tert-butyl pyridine is done into Spiro-OMeTAD to enhance the rate of hole extraction and transport. The additive doping of lithium bis(trifluoro methyl sulfonylimide) salt (Li-TFSI) and 4-tert-butyl pyridine (TBP) deteriorates the stability of MASnI₃ perovskite device than H-TFSI. In another approach, also Spiro-OMeTAD used as a HTM is doped with lithium bis(trifluoro methyl sulfonylimide) and 2,6-lutidine in order to enhance its hole mobility.

The solar cell capacitance simulator and analytical calculations (SCAPS) have reported an efficiency of above 15% in lead-free tin-based MASnI₃ perovskites employing Spiro-OMeTAD as a hole transport material. Chlorobenzene (CB), Li-TFSI, and TBP have been used as an additive in Spiro-OMeTAD in lead-free MA₃Bi₂I₉ perovskites. Oxygen-doped Spiro-OMeTAD employed as a HTM in Cs₃Bi₂I₉ perovskite solar device has yielded the maximum of the reported solar power conversion efficiencies. The Spiro-OMeTAD as a HTM has been used in lead-free tin, germanium, antimony, bismuth, and copper-based perovskite devices. Figure 3 shows the scanning electron microscopy (SEM) image of a MASnI₃ perovskite device with Spiro-OMeTAD as a HTM.

Cu-based lead-free perovskites reported so far have a planar heterojunction (n-i-p) structure employing Spiro-OMeTAD as a HTM with a highest reported efficiency of 2.41%. The low efficiency is attributed to the mismatch in the energy levels between the (MA)₂CuClX and Spiro-OMeTAD as a HTM leading to a poor hole extraction in the device. Another polymeric organic HTM PTAA has been employed in planar heterojunction n-i-p perovskite devices. Owing to its large mobility the use of PTAA as a HTM in Cs₃Bi₂I₉ perovskite solar cells has reported a V_OC of 250–300 mV and an extremely low solar power conversion efficiency. The doping of bismuth-based perovskite Cs₃Bi₂I₉ films with N,N-dimethyl formamide/hydroiodide (HI) solution featured a pure crystalline film with an excellent thermal stability. PTAA employed as a HTM in ethylene diammonium and methylammonium tin iodide en[MASnI₃] has reported a SPCE of 6.63% with a very high current density of 24.3 mA cm⁻² in a device architecture of FTO/C-TiO₂/mp-TiO₂/en[MASnI₃]/PTAA/Au.

Many research groups have synthesized lead-free MASnI₃, FASnI₃, and CsSnI₃ perovskite solar devices by using PTAA as a HTM. The presence of another polymeric organic poly(3-hexyl thiophene) (P3HT) as a HTM in lead-free perovskites can enhance the SPCE as well as stability of the fabricated device due to its potential to decrease the resistance from the hole transfer impedance. P3HT has been employed as a HTM instead of Spiro-OMeTAD for Cs₃Bi₂I₉ perovskite solar devices. In another research, P3HT has been used as a HTM in thin films of CsBiI₉ perovskite deposited by solution processing in device architecture of glass/FTO/compact TiO₂/mesoporous TiO₂/CsBiI₉ light absorber/P3HT/Ag. The addition of dopant 4-tert-butyl pyridine in Spiro-OMeTAD employed as a HTM in CsBiI₁₀ perovskite dissolves the light absorbing perovskite layer and suffers from stability and degradation issues. Unlike Spiro-OMeTAD, P3HT enhances the SPCE of the fabricated perovskite device as in CsSnBr₃ films, an efficiency of 0.11% was enhanced to 3.2% by replacing Spiro-OMeTAD HTM by P3HT. Also, P3HT employed as a HTM in MA₃Bi₂I₉ films enhances the overall performance of the fabricated device. P3HT has been employed as a HTM in MASnI₃, FASnI₃, CsSnI₃, en[MASnI₃], Cs₂SnI₆, MA₃Bi₂I₉, Cs₁Bi₂I₉, Cs₁Bi₁I₁₀, AgBiI₃, and AgBiI₅ perovskite solar devices.

In an inverted planar (p-i-n) perovskite device, the hole transport layer is kept under the perovskite light absorber layer that alleviates the stringent requirement of efficient conductivity of hole transport material. Polymeric organic HTM PEDOT:PSS is used in such devices. PEDOT:PSS is used as a HTM in FASnI₃ perovskite solar cells in an inverted planar (p-i-n) architecture and at present has reported a maximum SPCE of 8.12% in FA₀.₇₅MA₀.₂₅SnI₃ in lead-free tin-based perovskite with a V_OC of 0.61 V. The PEDOT:PSS with intercalated polyethylene glycol (PEG) used as a HTM in FASnI₃ perovskite solar cell alleviates the energy level mismatch between the perovskite light absorber and PEDOT:PSS as HTM. As a consequence, the SPCE increased from 2.01 to 5.12% in the forward scan. The inverted planar (p-i-n) device structure employed for antimony-based MA₃Bi₂I₉ perovskite films has reported a SPCE of 0.5% with a V_OC of 0.89 V. Additives are added into PEDOT:PSS in order to enhance the conductivity and morphology of PEDOT:PSS films. Polyorganic solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and ethylene glycol (EG) are used as additives to PEDOT:PSS to enhance its conductivity and improve its morphology.
glycol have been used as additives in lead-free perovskite device fabrication.\textsuperscript{148} The addition of additive in PEDOT:PSS films leads to enhancement in efficient hole extraction and collection rate attributed to the strong dipole–dipole or dipole–charge interactions between the polar additive and PEDOT:PSS used as a HTM in fabricated perovskite device.\textsuperscript{149} PEDOT:PSS as a HTM has been employed in lead-free MASnI\textsubscript{3}, FASnI\textsubscript{3}, FASnI\textsubscript{3}Br, FA\textsubscript{1-x}MA\textsubscript{x}SnI\textsubscript{3}, MA\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9}, MA\textsubscript{3}Sb\textsubscript{2}I\textsubscript{9}, and Cs\textsubscript{3}Sb\textsubscript{2}I\textsubscript{9} reported perovskite solar devices. Figure 4 shows the device structure and energy band diagram of (FA)\textsubscript{x}(MA)\textsubscript{1-x}SnI\textsubscript{3} perovskite solar cell.\textsuperscript{150} The use of Spiro-OMeTAD as a HTM damages the perovskite film. In order to overcome this issue, inverted planar (p-i-n) perovskite solar cells of MASnI\textsubscript{3} have been prepared by using PEDOT:PSS doped with poly-TPD as a HTM as shown in Figure 4.\textsuperscript{150} Figure 4 shows the (a) schematic device structure of (FA)\textsubscript{x}(MA)\textsubscript{1-x}SnI\textsubscript{3} perovskite solar cell, (b) band alignment diagram, and (c) cross-sectional SEM image of a completed device (scale bar: 500 nm).\textsuperscript{150} Addition of poly-TPD layer into PEDOT:PSS resulted into suppressed charge recombination and better efficiencies.\textsuperscript{151}

Besides organic HTMs, inorganic NiO (nickel oxide) and CuI (copper iodide) have also been used as a HTM in inverted planar (p-i-n) structures. NiO has a large work function of 15.2 eV in comparison to 5.2 eV for PEDOT:PSS that makes it viable for use as a HTM in perovskite solar cells reporting a higher \( V_{OC} \).\textsuperscript{152–155} The thickness and morphology of NiO as a HTM has a direct impact on charge collection and recombination in perovskite solar devices. The use of NiO as a HTM leads to more air stability in FASN\textsubscript{1}\textsubscript{3} perovskite inverted planar (p-i-n) solar cell using (PEA)\textsubscript{2}FA\textsubscript{8}Sn\textsubscript{9}I\textsubscript{28} as a light absorber reporting a SPCE of 5.94%.\textsuperscript{156} NiO\textsubscript{x} has been employed as a HTM in fabrication of CsSnI\textsubscript{3} perovskite solar cells reporting a \( V_{OC} \) of 0.55 V and enhanced air stability.\textsuperscript{159} Figure 5 shows the device architecture of CsSnI\textsubscript{3} using CuI as a HTM and SEM image of CsSnI\textsubscript{3} films.\textsuperscript{159} Perovskite solar cells without a HTM layer have the advantage of having simple structures, easy fabrication process, and higher stability if the work function of the metal electrode used in perovskite solar cells is close to the maximum valence band of perovskite light absorber, then absence of hole transport layer has no impact on the built-in electric field.\textsuperscript{160} The perovskite material in HTL-free devices works as a light absorber and a hole transport layer in such cells.\textsuperscript{161} A HTL-free solar cell of MASnI\textsubscript{3} has reported an efficiency of 3.15%. \( J_{SC} \) of 21.4 mA cm\textsuperscript{-2} that has been prepared through a solvent engineering method having a device architecture of the form FTO/c-TiO\textsubscript{2}/mp-TiO\textsubscript{2}/MASnI\textsubscript{3} light absorber/Au.\textsuperscript{162}

Figure 4. a) Schematic device structure of (FA)\textsubscript{x}(MA)\textsubscript{1-x}SnI\textsubscript{3} perovskite solar cell. b) Band alignment diagram. c) Cross-sectional scanning electron microscope (SEM) image of a completed device (scale bar: 500 nm). Reproduced with permission.\textsuperscript{150} Copyright 2017, Wiley-VCH.

Figure 5. A) Scheme of the “inverted” structure planar B-\( \gamma \)-CsSnI\textsubscript{3} PSC device employing NiO\textsubscript{x} as HTL and PCBM as ETL, and B) corresponding energy level diagram (the dashed line indicates NiO\textsubscript{x} work function). Reproduced with permission.\textsuperscript{157} Copyright 2016, Wiley-VCH.
HTL-free CsSnI$_3$ PSC has stability ten times greater than the devices using same device architecture using MAPbI$_3$ as a light absorber.[163] Inorganic metal oxides like TiO$_2$, ZnO, SnO$_2$ and organic fullerene derivatives like phenyl-C$_{60}$-butynic and methyl ester (PC$_{60}$BM) or PC$_{70}$BM have been employed as an ETM for perovskite solar cells. The efficient ETM should have the capability to engineer the optical bandgap for maximum absorption of incident light by the perovskite light absorber layer and must have a better electron extraction and hole blocking property in order to suppress the electron–hole recombination at the interface of the device. TiO$_2$ as an ETM has been employed in device fabrication of most of the reported lead-free perovskite solar cells. On the top of a mesoporous TiO$_2$ layer, the perovskite film of MASnI$_3$ is crystallized upon spin-coating and it penetrates into the pores of ETM. The MASnI$_3$ films fabricated on the top of 400 nm thick mp-TiO$_2$ layer are better than that of prepared on an 80 nm thick mp-TiO$_2$ layer. The mesoporous MAPbI$_{3-x}$Cl$_x$ perovskite films have a better film morphology than that of MASnI$_3$ films fabricated in a similar way and architecture as shown in Figure 7. Figure 8 shows the schematic energy-level diagram of CH$_3$NH$_3$SnI$_{3-x}$Br$_x$ compounds.[106]

By controlled crystallization, it is possible to enhance the quality of film formation.[120] In another approach, solvent engineering method was employed to prepare thin films of MASnI$_3$. A 30 nm thick TiO$_2$ compact layer as an ETM is deposited on the substrate by atomic layer deposition system. The perovskite light absorber crystals infiltrate into the pores of mp-TiO$_2$ layer and remaining pores of mesoporous TiO$_2$ layer are filled up by the HTM forming a 200 nm thick capping layer on the top of the composite structure.[106]

In a planar heterojunction (n-i-p) structure, a compact TiO$_2$ layer is deposited on a glass that is further covered by a mesoporous TiO$_2$ layer in order to enhance the electron collection and to avoid hysteresis loss during V–I measurements.[164] By employing mp-TiO$_2$ as an ETM, the homogenous MASnI$_3$ films prepared by vapor-assisted solution process[165,166] have reported a $J_{SC}$ of 17.4 mA cm$^{-2}$ when used as a light absorber in perovskite solar cells. The SPCE of pristine FASnI$_3$ films was 0.003% by using mesoporous TiO$_2$ layer as an ETM. The low value of SPCE is attributed to high background carrier density of 10$^{19}$ cm$^{-3}$ that leads to a metal like conductivity and device short circuiting.[156] However, the addition of Br$_2$ into FASnI$_3$
As a consequence of reduction in tin vacancies, the leakage current of the device is reduced that further increases the recombination lifetime and finally $V_{OC}$ and FF of the fabricated device and SPCE up to 5.5%.\cite{167} TiO$_2$ as an ETM has an intrinsic low mobility and this has been a generation of deep traps by UV light that results in charge accumulation, recombination classes, and severe $V-I$ hysteresis.\cite{41,59,62,168,169} The evaporation-assisted method combining thermal evaporation and ion beam sintering and exhibits degradation in SPCE on exposure to UV light. TiO$_2$ requires high-temperature annealing but the substrate cannot withstand such a high temperature. The mesoporous TiO$_2$ (n-i-p) devices have exhibited better efficiencies whereas inverted planar (p-i-n) devices suffer from hysteresis losses. Tin-based lead-free perovskites are considered unsuitable for planar heterojunction solar cells due to their short diffusion lengths, a SPCE of 1.72% is shown by FASnI$_3$Br films as a light absorber with C$_{60}$ as ETM suggesting the significance of perovskite film morphology on the device performance. FASnI$_3$Br films with an architecture ITO/PEDOT:PSS/FASnI$_3$Br/ C$_{60}$/Ca/Al reported a $J_{SC}$ of 6.82 mA cm$^{-2}$ and $V_{OC}$ of 0.46 mV.\cite{171} Figure 9 shows the structure of (a) FASnI$_3$Br (SEM image)\cite{171} and (b) FASnI$_3$ (SEM image) and energy band diagram.\cite{172}

Anatase, rutile, and brookite are three stable phases in TiO$_2$ when used as an ETM. For anatase TiO$_2$-based perovskite solar cells, the electron diffusion constant was ten times higher but the time constant for recombination was ten times lower than for rutile TiO$_2$-based one. Fast charge recombination in anatase TiO$_2$-based device is the result of poor charge separation in TiO$_2$/perovskite interface.\cite{173} Figure 10 shows the MBI perovskite skelton deposited on a compact, mesoporous, and brookite TiO$_2$.\cite{174} Fullerene C$_{60}$ and its derivatives such as PC$_{60}$BM or PC$_{70}$BM have been employed as an interfacial material at the interface between TiO$_2$ and perovskite layer because of its high electron mobility. A self-assembled C$_{60}$ monolayer was introduced on TiO$_2$ surface that enhances the charge separation, reduces the capacitance of TiO$_2$ and $V-I$ hysteresis.\cite{175} Organic ETM of PC$_{60}$BM or PC$_{70}$BM is more efficient to collect electrons in comparison to mp-TiO$_2$ in inverted planar p-i-n devices as they can passivate the charge traps of metal oxide.\cite{176–178} and hence can reduce the nonradiative recombination channels at the surface leading to an improved SPCE with a very low hysteresis.\cite{179,180} The perovskite layer of Cs$_3$Sb$_2$I$_9$ was prepared through a single-step spin-coating process for an inverted planar p-i-n structure using architecture glass/ITO/PEDOT:PSS/(NH$_4$)$_3$Sb$_2$I$_9$/PC$_{71}$BM/C$_{60}$/bathocuproine (BCP)/Al.\cite{159} PC$_{70}$BM/C$_{60}$ is a double fullerene layer employed as an ETM to minimize the trap densities.\cite{181} Also, the perovskite solar cells with a p-i-n structure of ITO/PEDOT:PSS/(NH$_4$)$_3$Sb$_2$I$_9$/ PC$_{60}$BM/Al were synthesized to study the photovoltaic performance of (NH$_4$)$_3$Sb$_2$I$_9$ reporting a SPCE of 0.51%.\cite{147}

The selection of charge extraction layers by modulating a desirable energy band alignment between the conduction band edge of CsSnI$_3$ and LUMO of ETL is another feasible strategy. A $V_{OC}$ of 0.55 V was reported for CsSnI$_3$ perovskite solar device using p-i-n structure ITO/CuI/CsSnI$_3$/indane-C$_{60}$bisadduct ICBA/BCP/Al architecture. Here, ICBA acted as an ETM.\cite{159} BCP is used as an interfacial material in between C$_{60}$ derivatives and the metal electrodes. The FF was significantly improved by using electrode interfacial layer. In an inverted planar (p-i-n) FASnI$_3$ perovskite device, C$_{60}$ has been employed as an ETM for efficient electron extraction.\cite{172} A solution gel derived ZnO used as an ETL bilayer fabricated at $<110$ °C facilitates the improved energy level alignment and enhanced charge carrier extraction and a PCBM layer is used to reduce the hysteresis and enhance the perovskite thermal stability.

ZnO can be a potential candidate to replace TiO$_2$ as an ETL layer without causing a marked effect on the performance of PSCs.\cite{182,183} The doping of pure ZnO nanorods with Au/Al results in high electron mobility and high electron density.\cite{184}
Figure 9. a) Configuration of the FASnI$_2$Br-based p-i-n heterojunction solar cells and its cross-sectional SEM image of a typical device. Reproduced with permission.\cite{171} Copyright 2016, Springer Nature. b) Cross-sectional SEM image of the entire device with 10 mol% SnF$_2$ additives, in which each layer is labeled, and schematic of energy level diagram of our FASnI$_3$ perovskite solar cells. Reproduced with permission.\cite{172} Copyright 2016, Wiley-VCH.

Figure 10. Top and cross-sectional SEM view of MBI perovskite layer deposited on a,b) TiO$_2$ compact layer and c,d) brookite mesoporous layer. Reproduced with permission.\cite{174} Copyright 2016, American Chemical Society.
From SCAPS-1D, the use of ZnO nanorods as an ETM and Cu$_2$O as a HTM for MASn$_3$ perovskite devices has displayed the best performance among all the PSCs. Cu$_2$O is a suitable HTM layer in PSCs due to its high hole mobility and low electron affinity. The device displayed a maximum SPCE for ZnO nanorods/MASn$_3$/Cu$_2$O structure exhibiting a $J_{SC}$ of 32.26 mA cm$^{-2}$, $V_{OC}$ of 0.85 V, FF of 0.74, and SPCE of 20.23%.\cite{185} The ETM used in a perovskite solar cell has a significant impact on the SPCE of the device when bl-TiO$_2$ layer in Ag$_2$BiI$_4$ is replaced by bl-SnO$_2$, there is a significant increase in current density from 1.33 mA cm$^{-2}$ (TiO$_2$) to 2.31 mA cm$^{-2}$ (SnO$_2$) attributed to better electron extraction by SnO$_2$ ETM.\cite{186}

7. Lead-Free Perovskites

7.1. Tin-Based Perovskites

Tin is the most suitable candidate for substitution of lead for lead-free perovskite solar cell because of its similar valence electronic configuration as that of lead and approximate same ionic radius of Sn$^{2+}$ (115 pm) as that of Pb$^{2+}$ (119 pm). It has lower value of electronegativity Sn$^{2+}$ (1.96) than that of Pb$^{2+}$ (2.33).\cite{217} Tin-based perovskites have optical bandgap of 1.2–1.6 eV most suitable for their use as light absorbers, large carrier mobilities, and low exciton binding energies of 18 meV.\cite{105,119,187} Tin-based perovskites are represented by the general formula ASnX$_3$ where A can be MA$^+$, FA$^+$ or Cs$^+$ cation, and X is a halogen anion.

Methylammonium tin halides MASnX$_3$ have a direct bandgap of 1.20–1.35 eV, electron mobility of 2320 cm$^2$ V$^{-1}$ s$^{-1}$, hole carrier mobility of 322 cm$^2$ V$^{-1}$ s$^{-1}$, and long charge carrier diffusion length of more than 500 nm.\cite{117} The first completely lead-free Sn-based perovskite MASn$_3$I$_3$ was processed on a mesoporous TiO$_2$ scaffold that achieved SPCE of 8.4% under 1 sun illumination in a highly inert atmosphere in a glove box with $V_{OC}$ of 0.88 V, $J_{SC}$ of 16.8 mA cm$^{-2}$, and FF of 0.42 obtained from material having optical bandgap of 1.23 eV.\cite{120} A Sn-based perovskite model with the novel architecture of glass/ZnO:Al/TiO$_2$/CH$_3$NH$_3$SnCl$_3$/Cul/Au, devised by Mandadapu et al.,\cite{189} has been analyzed using the solar cell capacitance simulator (SCAPS-1D), with the predicted parameters such as thickness 0–6 μm, defect density of 10$^{14}$ cm$^{-3}$ of light absorber layer, and bandgap 1.3 eV. The model achieved a SPCE of 24.82%, $V_{OC}$ of 1.04 V, $J_{SC}$ of 3.50 mA cm$^{-2}$, and FF of 0.78. The excellent results of this model clearly signify the enormous potential of Sn-based perovskites for their efficient use in solar cells. Since then an extensive work has been carried out on preparation and characterization of Sn-based perovskites material to examine their structural, optical, and charge transport abilities for efficient use as light absorber in perovskite solar cells.\cite{188} The perovskite solar cells with CH$_3$NH$_3$SnBr$_3$ as light absorber reported a SPCE of 0.35% for coevaporation and 0.12% for sequential deposition method.\cite{190} The composition of a halide anion in mixed halide tin-based perovskites has an influence on the photovoltaic performance exhibited by them. The mixed halide tin-based perovskite MASn$_{1-x}$Br$_x$ was investigated by altering the Br$^-$/I$^-$ ratio, it was reported that MASnBr$_3$ as a light absorber displays more $V_{OC}$ (0.88 V) and less $J_{SC}$ (8.26 mA cm$^{-2}$) in comparison to MASnBr$_2$ having $V_{OC}$ (0.82 V) and $J_{SC}$ (12.33 mA cm$^{-2}$). Among all MASn$_{1-x}$Br$_x$ perovskites, MASnBr$_2$ has the highest reported SPCE of 5.73% under stimulated full sunlight.\cite{192} Also, the position of band edge of mixed halides perovskites, MASn$_{1-x}$Br$_x$ can be tuned from 954 nm (MASn$_1$I$_3$) to 577 nm (MASnBr$_3$) thus displaying a remarkable tunability of color. Also the mixed halides tin-based perovskites MASnBr$_2$Cl$_x$ have been fabricated for carbon-based mesoscopic cells devoid of ETM and HTM layers by varying the composition of SnCl$_2$/SnBr$_2$. The solar device with MASnBr$_{1.8}$Cl$_{0.2}$ achieved the best photovoltaic performance of 3.11% with a long-term stability in air. The device exhibited excellent charge recombination and dielectric relaxation properties.\cite{193} However, tin-based perovskites have low values of SPCE due to fast oxidation of divalent Sn$^{2+}$ into a more stable state Sn$^{4+}$ and easy formation of Sn vacancies due to small value of formation energy. As a consequence of it, there is a large charge carrier recombination and high levels of self-p-doping in Sn-based perovskite films. Thus, a lot of research has been carried out to suppress oxidation of divalent Sn$^{2+}$. SnF$_2$ has been added to such films to inhibit the oxidation process so as to reduce the background carrier hole density by filling Sn vacancies. The entire fabrication process is carried out in an inert atmosphere in the glove box encapsulated by hot melt polymer film, a glass cover slide with sealed edges so as to avoid the oxidation of perovskite film on exposition to ambient air that could cause its fast degradation. Addition of 5-ammonium valeric acid iodide to MASn$_3$I$_3$ suppressed oxidation of Sn$^{4+}$ for better stability of the perovskite device.\cite{192} Hypophosphorous acid was also used for reducing the oxidation of divalent Sn$^{2+}$ thereby reducing the number of Sn vacancies and charge carrier density. As a consequence of it, there is enhancement in charge recombination lifetime by fourfold than that of the control device.\cite{193}

A SPCE of 2.14% was reported for a perovskite solar cell having MASn$_3$I$_3$ with SnF$_2$ additive as a light absorber. The fabricated device achieved $V_{OC}$ of 0.45 V, $J_{SC}$ of 11.48 mA cm$^{-2}$, and FF of 0.48 and has long lifetimes of 200 h under 1 sun degradation conditions.\cite{194} However, an excess of SnF$_2$ deteriorates the perovskite film morphology and device performance indicating that SnF$_2$ concentration must be kept very low; as a result, the background charge carrier density remains too large to achieve high efficiency, thus it becomes mandatory to explore new and more efficient ways to alleviate the background charge carrier density for better performance of the perovskite solar cell. It was also proposed that the fabrication of perovskite film must be carried out under a reducing vapor atmosphere to reduce the hole density in MASn$_3$I$_3$ films by inhibiting the oxidation of Sn$^{2+}$ during the fabrication process. The excess use of SnF$_2$ induces the phase separation in perovskite films. As a result of exposure to excess SnF$_2$, plate like aggregates are formed in the film, thus it was resolved to use nonsolvent dripping process along with SnF$_2$ via the formation of SnF$_2$-pyrazine complex. Pyrazine has a strong binding affinity to SnF$_2$ thereby suppressing the phase separation induced by the excess use of SnF$_2$.\cite{195} Table 4 shows some photovoltaic parameters of methylammonium tin halides.

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Formamidinium tin iodide FASnI$_3$ has a direct bandgap of 1.41 eV closer to the requisite bandgap value for use in perovskite solar cells and do possess a single stable phase over a broad temperature range up to 200 °C. Sn-based perovskite FASnI$_3$ is more stable than MASnI$_3$ due to suppression of oxidation of Sn$^{2+}$ by FA$^+$.\cite{188,200} FASnI$_3$ is first used as light absorber in perovskite solar cell by Koh et al.\cite{109} The fabricated films displayed a SPCE of 2.1%, $J_{SC}$ of 24.5 mA cm$^{-2}$, $V_{OC}$ of 0.2 V, and FF of 0.36. Additive SnF$_2$ is incorporated into FASnI$_3$ to suppress the oxidation of Sn$^{2+}$ for better film morphology. A SPCE of 4.8% has been achieved by incorporating SnF$_2$ in FASnI$_3$ to form a complex with SnF$_2$ thereby improving the morphology of the perovskite film and slowing down the rate of crystallization of perovskite thin film. Antisolvent process can play a very significant role in preparing the perovskite solar cell with an invested structure. By tuning the ratio of FA and MA yields the different values of SPCE. A SPCE of 7.1% and retained 96% of its initial efficiency over 100 d maintaining 98% of their initial performance.\cite{195} Chlorobenzene is also used as an antisolvent for FASnI$_3$ films. The A-site cation in Sn-based perovskite has a significant effect on photovoltaic performance. The use of diethylammonium (en) and FA$^+$ at A-site of tin-based perovskite results in a wider bandgap and an improved stability of photovoltaic performance. The complex en [FASnI$_3$] displayed a SPCE of 7.1% and retained 96% of its initial efficiency over 1000 h without encapsulation. Also, the addition of en at A-site cation along with (FA/MA/Cs) Sn$_3$ cannot reduce dimensionality of the perovskite to 2D.\cite{192}

The first mixed design composition in tin-based perovskite was reported on FA$_{1-x}$MA$_x$SnBr$_3$ with a cubic structure. The bandgap of the perovskite film was varied from 2.4 eV ($x = 0$) to 1.92 eV ($x = 0.82$) but the device displayed no photovoltaic performance.\cite{201} Another mixed A-site cation perovskite (FA)$_x$(MA)$_{1-x}$SnI$_3$ has been investigated for its use as a light absorber in a perovskite solar cell with an invested structure. By tuning the ratio of FA and MA yields the different values of SPCE. A SPCE of 8.12% is achieved for (FA)$_{0.75}$(MA)$_{0.25}$SnI$_3$ with $V_{OC}$ of 0.61 V and bandgap of 1.33 eV. The high SPCE is attributed to the morphology of FASnI$_3$ perovskite that achieved a SPCE of 4.8%, $V_{OC}$ of 0.32 V, $J_{SC}$ of 23.7 mA cm$^{-2}$, and improved stability. The encapsulated FASnI$_3$ films displayed a stable performance for over 100 d maintaining 98% of their initial efficiency.\cite{195}

| Light absorber | $E_g$ | $V_{OC}$ | $J_{SC}$ | FF | SPCE | Architecture | Ref. |
|----------------|------|---------|---------|----|------|-------------|-----|
| FASnI$_3$      | 1.23 | 0.88    | 16.8    | 0.42 | 6.4  | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/Spiro-OMeTAD/Au | [120] |
| MASnI$_3$      | 1.3  | 0.716   | 15.18   | 0.50 | 5.44 | FTO/c-TiO$_2$/absorber/Spiro-OMeTAD/Au | [196] |
| MASnI$_3$+SnF$_2$ | 1.3  | 0.32    | 21.4    | 0.46 | 3.15 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber | [162] |
| MASnI$_3$      | 1.3  | 0.38    | 12.1    | 0.36 | 1.7  | ITO/PEDOT:PSS/poly-TPD/absorber/C$_{60}$/BCP/Ag | [151] |
| MASnI$_3$      | 1.26 | 0.27    | 17.4    | 0.39 | 1.86 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber | [197] |
| MASnBr$_2$     | 1.75 | 0.82    | 12.33   | 0.57 | 5.73 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/Spiro-OMeTAD/Au | [106] |
| MASnBr$_2$     | 2.15 | 0.88    | 8.26    | 0.59 | 4.27 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/Spiro-OMeTAD/Au | [106] |
| MASnBr$_2$     | 2.2  | 0.50    | 4.27    | 0.49 | 1.12 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/P3HT/Au | [190] |
| MASnBr$_3$     | 1.41 | 0.20    | 4.5     | 0.36 | 0.3  | ITO/PEDOT:PSS/absorber/C$_{60}$/Ag | [198] |
| MASnI$_3$+hydrazine vapor | 1.3  | 0.38    | 19.9    | 0.51 | 3.80 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/P3HT/Au | [199] |
| MASnI$_3$+SnF$_2$ | –    | 0.45    | 11.8    | 0.40 | 2.14 | FTO/PEDOT:PSS/absorber/C$_{60}$/BCP/Au | [194] |
| en[MASnI$_3$]+SnF$_2$ | 1.4  | 0.43    | 24.3    | 0.63 | 6.63 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/P3HT/Au | [142] |
| MASnI$_3$+SnF$_2$ | 0.46 | 21.4    | 0.42    | 1.29 | 6.92 | ITO/PEDOT:PSS/absorber/C$_{60}$/BCP/Au | [150] |
| (FA)$_{0.75}$(MA)$_{0.25}$SnI$_3$ | 1.33 | 0.61    | 21.2    | 0.62 | 8.12 | ITO/PEDOT:PSS/absorber/C$_{60}$/BCP/Au | [150] |
| (FA)$_{0.75}$(MA)$_{0.25}$SnI$_3$ | 1.33 | 0.53    | 21.3    | 0.52 | 5.92 | ITO/PEDOT:PSS/absorber/C$_{60}$/BCP/Au | [150] |
| FASnI$_3$      | 1.36 | 0.48    | 21.3    | 0.64 | 6.60 | ITO/PEDOT:PSS/absorber/C$_{60}$/BCP/Au | [150] |
| MASnBr$_2$.Cl$_x$+0%SnCl$_3$+100% SnBr$_2$ | 1.81 | 0.31    | 13.37   | 0.52 | 2.18 | Glass/FTO/TiO$_2$/absorber/carbon | [191] |
| 10% SnCl$_3$+90% SnBr$_2$ | 1.87 | 0.38    | 13.99   | 0.57 | 3.11 | Glass/FTO/TiO$_2$/absorber/carbon | [191] |
| 25% SnCl$_3$+75% SnBr$_2$ | 1.97 | 0.35    | 11.06   | 0.47 | 1.87 | Glass/FTO/TiO$_2$/absorber/carbon | [191] |
| 50% SnCl$_3$+50% SnBr$_2$ | 1.49 | 0.24    | 9.33    | 0.47 | 1.07 | Glass/FTO/TiO$_2$/absorber/carbon | [191] |
| 75% SnCl$_3$+25% SnBr$_2$ | 1.36 | 0.19    | 13.34   | 0.32 | 0.81 | Glass/FTO/TiO$_2$/absorber/carbon | [191] |
| 100% SnCl$_3$+0% SnBr$_2$ | 1.25 | 0.12    | 19.12   | 0.30 | 0.74 | Glass/FTO/TiO$_2$/absorber/carbon | [191] |

$J_{SC}$, $V_{OC}$, FF, and SPCE are short for short circuit current density, open circuit voltage, fill factor, and power conversion efficiency, respectively.
achieved a SPCE of 9% with a FASnI3 perovskite solar cell can improve the morphology of the perovskite films, inhibition of oxidation of Sn2+ that enable better separation of charge carriers and suppression of oxidation of Sn2+ into Sn4+, and passivation of surface defect states. The 1% EDAI2-doped FASnI3 perovskite films displayed an efficiency of 8.9% with a stability of over 1400 h with only slight degradation for more than 200 h in contrast to pristine FASnI3 films with a SPCE of 7.4% only. The high efficiency is attributed to improved perovskite film morphology and passivation of surface defects that enable better separation of charge carriers and suppression of oxidation of Sn2+ into Sn4+. [203] Figure 11a shows the schematic representations of perovskite crystals in the presence of BAI and EDAI3 additives; top-view SEM images of (b) pristine FASnI3, (c) FASnI3-BAI 15%, and (d) FASnI3-EDA12 1%; (e) current–voltage curves, (f) corresponding IPCE spectra with integrated current densities, (g) histograms of 30 fresh cells fabricated under the same experimental conditions, (h) Mott–Schottky plots, (i) Nyquist plots obtained from electrochemical impedance spectra (EIS), and (j) stabilized power-conversion efficiencies and photocurrent densities of the devices having M-TiO2 as electron transport layer. The fabricated devices achieved SPCE of 5.5% with high stability of encapsulated devices over 1000 h under continuous illumination including UV region. [162] Table 5 shows some photovoltaic parameters of formamidinium tin halides.

Cesium tin iodide perovskite CsSnI3 possess a direct bandgap of 1.30 eV, a melting point of 435 °C indicating its better thermal stability and a 3D orthorhombic structure whereas cesium tin bromide perovskite CsSnBr3 has a bandgap of 1.7 eV [102] Cesium-based tin perovskite has a high hole mobility of 585 cm-1 V-1 s-1, low exciton binding energy (180 meV) than MAPbI3. [119,187] The melt-synthesized CsSnI3 ingots containing high-quality large single crystal grains have been reported to have bulk carrier lifetime more than 6.6 ns, doping concentration of about 4.5 × 1017 cm-3, and minority carrier diffusion lengths approaching to 1 μm. [118] A SPCE of 23% was predicted for optimized single crystal solar cells CsSnI3 highlighting their great potential for use in perovskite solar cell. The CsSnI3 was first used in a Schottky-type perovskite solar cell consisting of simple layer architecture of ITO/CsSnI3/Au/Ti on a glass substrate that achieved an efficiency of 0.9%. A HTM-free CsSnI3 perovskite solar cell with SnI2 as an additive displayed an efficiency of up to 2.76% with a VOC of 0.43 V and FF of 0.39. [212] The use of excess SnI2 as an additive in CsSnI3 not only suppress Sn4+ vacancies but also reduces p-type conductivity thereby producing a SPCE of 4.8% in CsSnI3 perovskite solar cells. [213] The thin films of CsSnBr3 were fabricated with the addition of hypophosphorous acid (HPA) with thermal stability and accumulation and recombination in the device is suppressed leading to a high SPCE of 7.05%. [204]

The bifunctional ammonium cations, 2-hydroxyethyl ammonium OH(CH2)NH3+(HEA)+, are incorporated into FASnI3 resulting in a mixed tin-based perovskite HEA2FAxSnI3−x where x = 0–1 and can act as a light absorber in carbon-based mesoscopic solar cells. As a consequence of incorporation of HEA+, the crystal lattice changed from orthorhombic to rhombohedral (x = 0.2–0.4). For x ≥ 0.6, a 3D vacant perovskite (HEA)2FA−xSnI3+x with a tetragonal structure is formed. The light absorbers in this series are synthesized by employing mesoporous solar cells using one-step drop-cast (DC), two-step solvent–solvent extraction (SE), and a solvent extraction by using ethylenediammonium diiodide (EDA1) as an additive. The fabricated solar device HEA2FAxSnI3 displayed the photovoltaic parameters with VOC of 0.371 V, JSC of 18.52 mA cm−2, FF of 0.562, and a stable SPCE of 3.9% for a period of 340 h. [205] The FASnI3 perovskite light absorbers incorporated with a diammonium cation such as propylenediammonium (PW) and trimethylenediammonium (TN) display better efficiency than the pristine FASnI3 solar cell. The FASnI3 light absorbers mixed with 10% TN and 10% PN displayed a SPCE of 5.53 and 5.58% with a better film morphology along with retaining their 3D perovskite structure. [206] Figure 11 shows the (k) device structure, (l) J–V curves, (m) EQE curves, and (n) PCE statistics of the FASnI3 solar cells with and without 10% PN and 10% TN. The addition of bromide into FASnI3 crystal lattice reduces the p-doping in the perovskite film by reducing the Sn vacancies thereby lowering the current density of the light absorbers. As a result, there is an enhancement in charge recombination lifetime that increases VOC and FF of the devices having M-TiO2 as electron transport layer. The fabricated devices achieved SPCE of 5.5% with high stability of encapsulated devices over 1000 h under continuous illumination including UV region. [162] Table 5 shows some photovoltaic parameters of formamidinium tin halides.
up to 473 K achieving a SPCE of 3% that last for over 77 d.[193]

The results of a computational study on mixed cesium perovskite Rb$_y$Cs$_{1-y}$Sn (Br$_x$I$_{3-x}$)$_3$ as a light absorber have revealed that the substitution of Rb$^+$ for Cs$^+$ enhanced the quality of perovskite film and its practical applicability in perovskite solar cells.[214] Another study on CsSnI$_3$ and CsSnI$_3-x$Br$_x$ as light absorbers in n-i-p devices structure reported an efficiency of 2%. CsSnI$_3$ has a small bandgap of 1.27 eV to a near-infrared absorption onset to 950 nm and exhibited a high charge carrier density up to 27.67 mA cm$^{-2}$.[215]

An excess of SnCl$_2$ and SnI$_2$ to CsSnI$_3$ perovskite films can have masked influence on both stability and SPCE of the corresponding cells reported to be of 3%. An extensive monitoring of oxidation of CsSnI$_3$ in the air by using additives SnCl$_2$, SnBr$_2$, and SnI$_2$ has been carried out to measure electronic, optical absorption spectrum with time and reported that it exhibits the highest stability by inhibiting the crystallization/decomposition.[163,192] The addition of SnF$_2$ lowers the background charge carrier density by neutralizing traps.[214,216] The mesostructured CsSnI$_3$ displayed a SPCE of 2.02% with the addition of 20% SnF$_2$ as an additive. Also a spectral response of 950 nm is demonstrated with SnF$_2$ addition. As a result, the concentration of the defect is reduced that further suppressed the background charge carrier density.[215] The anionic substitution of Br$^-$ in CsSnI$_3$-Br$_x$ (0 ≤ x ≤ 3) results in change in crystal structure from orthorhombic to cubic framework for CsSnBr$_3$ enhancing the $V_{OC}$ and $J_{SC}$ as a result of decrease in tin vacancies and low charge carrier densities of $10^{15}$ cm$^{-3}$.[217] The carrier lifetime gets enhanced and the PL line width has reduced when the temperature decreases below 110 K due to the phase transition from orthorhombic to tetragonal phase in CsSnX$_3$ that improved the solar cell performance.[218]

The evaporation method comprising of thermal evaporation with solution method has been used to produce smooth

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Figure 11. a) Schematic representations of perovskite crystals in the presence of BAI and EDAI$_2$ additives; top-view SEM images of b) pristine FASnI$_3$, c) FASnI$_3$-BAI 15%, and d) FASnI$_3$-EDAI$_2$ 1%; e) current–voltage curves, f) corresponding IPCE spectra with integrated current densities, g) histograms of 30 fresh cells fabricated under the same experimental conditions, h) Mott–Schottky plots, i) Nyquist plots obtained from electrochemical impedance spectra (EIS), and j) stabilized power-conversion efficiencies and photocurrent densities of the FASnI$_3$-BAI 15%and FASnI$_3$-EDAI$_2$ 1% devices for 240 s; Reproduced with permission.[203] Copyright 2018, Royal Society of Chemistry. k) Device structure, l) J–V curves, m) EQE curves, and n) PCE statistics of the FASnI$_3$ solar cells with and without 10% PN and 10% TN; Reproduced with permission.[206] Copyright 2018, American Chemical Society.
uniform dense pinhole-free CsSnI₃ films that achieved a SPCE of 1.86% with \( V_{OC} \) of 0.265 V, \( J_{SC} \) of 15.25 mA cm\(^{-2}\), and FF of 0.46, by using the architecture (FTO/bi-TiO₂/mp-TiO₂/absorber/Spiro-OMeTAD).\[106\]

The undesirable p-doping of CsSnI₃ perovskite films can be reduced by the addition of piperazine that can improve the morphology of the film as well as can alleviate the crystallization of excess SnI₂ at the same time. With the use of piperazine as an additive, CsSnI₃ perovskite devices displayed a SPCE of 3.83%.[219]

Table 6 shows some photovoltaic parameters of cesium-based perovskites. Figure 12 shows schematic diagram along with the performance of CsSnI₃-based perovskite solar cell.[170]

Tin in +4 oxidation state shows more air and moisture stability with enhanced photovoltaic properties. To combat the challenge of oxidation of Sn⁴⁺ to Sn⁶⁺, tin-based perovskite structures like \( A₂SnX₆ \) are investigated for their use in a perovskite solar cell.[105,216,225] Tin-based Cs₂SnI₆ as a light absorber was first studied in 2016 that reported an efficiency of 1%.[216,223] Cs₂SnI₆ do possess defects of iodide vacancies and interstitial Sn atoms that give rise to the intrinsic n-type behavior completely opposite to p-type behavior in CsSnI₃. Optimization of thickness of perovskite light absorption layers leads to spontaneous oxidation conversion of unstable B-YCsSnI₃ to air stable Cs₂SnI₆ that has bandgap of 1.48 eV and a high absorption coefficient of 10⁵ cm\(^{-1}\) eV\(^{-1}\). The bandgap of \( A₂SnX₆ \) perovskite depends upon the composition of halide anion. With increase in bromide composition CsSnI₄Br₂, the bandgap can be tuned from 1.3 to 2.9 eV and the color of the film changes from dark brown to brown red then to yellow. Cs₂SnI₆Br₂ reported an efficiency of 2.03% highest among all the fabricated compositions. The fabrication of all the reported composition was done in ambient air without the use of any additive and the perovskite film exhibited thermal stability.[226] The polycrystalline films of (MA)₂SnI₆ have been proposed by
using thermal evaporation method having a direct bandgap of 1.81 eV with a strong absorption coefficient of \(7 \times 10^4\) cm\(^{-1}\), carrier concentration of \(2 \times 10^{15}\) cm\(^{-3}\), and electron mobility of \(\approx 3\) cm\(^2\) V\(^{-1}\) s\(^{-1}\).[129]

Table 7 shows some photovoltaic parameters of cesium-based perovskites.

### 7.2. Germanium-Based Perovskites

Germanium is another candidate for substitution of lead for lead-free perovskite solar cells because of its valence electronic configuration as that of Pb\(^{2+}\). Ge\(^{2+}\) has a small ionic radius (73 pm) as compared to that of divalent metal cation Pb\(^{2+}\) (119 pm) and Sn (110 pm). Ge\(^{2+}\) is low in toxicity than Pb\(^{2+}\).[227] However, germanium is prone to oxidation than tin. It has a value of electronegativity (2.1) as compared to Pb (3.2) and Sn (1.96). Methyl ammonium germanium halides MAGe\(_X\) are the most potential candidate for perovskites solar cells as Goldschmidt tolerance factor for MAGe\(_X\)\([X-\text{Cl, Br, I}\] has value of 1.005, 0.988, and 0.965, respectively, that is close to the optimum range \(0.99 < t < 1.03\) for a material to form a stable 3D perovskite structure. MAGeI\(_3\) has an optical bandgap 1.63 eV which is greater in magnitude than that of MAPbI\(_3\) (1.55 eV) and MASnI\(_3\) (1.30), excellent hole and electron conducting behavior and better stability in air as compared to MaPbI\(_3\).[217] However, Ge\(^{2+}\) cation being smaller in size (73 pm) deviates from its regular [GeI\(_6\)] octahedral center as it replaces cation of much larger ionic radius as that of Pb\(^{2+}\) (119 pm) and Sn\(^{2+}\) (110 pm).[228]

![Figure 12. a) Schematic diagram for development of evaporation-assisted solution (EAS) method using CsSnI\(_3\). b) J–V curves of the device by EAS method in both forward and reverse directions, c) IPCE spectrum of the optimized device (\(V_{oc} = 0.265\) V, \(J_{sc} = 15.25\) mA cm\(^{-2}\), FF = 46.05\%, and PCE = 1.86\%), d) steady-state current density of champion device at a bias of 0.18 V, and d) PCE histogram of 25 tested devices. Reproduced with permission.[170] Copyright 2018, Wiley-VCH.](image-url)
Table 7. Photovoltaic parameters of tin-based perovskites A₂SnX₄.

| Light absorber | $E_g$ | $J_{SC}$ | $V_{OC}$ | FF | SPCE | Architecture | Ref. |
|---------------|-------|---------|---------|----|------|-------------|------|
| Cs₂SnI₄      | 1.48  | 5.41    | 0.51    | 0.35 | 0.96 | FTO/TiO₂/absorber/P3HT/Ag | [216]|
| Cs₂SnI₆      | 1.30  | 6.75    | 0.37    | 0.59 | 1.47 | FTO/bl-TiO₂/2% Sn-TiO₂/absorber/Cs₂SnI₆-HTM/LPAH/FTO | [226]|
| Cs₂SnI₅Br₂   | 1.38  | 6.58    | 0.44    | 0.55 | 1.60 | FTO/bl-TiO₂/2% Sn-TiO₂/absorber/Cs₂SnI₅Br₂/HTM/LPAH/FTO | [226]|
| Cs₂SnI₅Br₄   | 1.40  | 6.23    | 0.36    | 0.57 | 2.03 | FTO/bl-TiO₂/2% Sn-TiO₂/absorber/Cs₂SnI₅Br₄/HTM/LPAH/FTO | [226]|
| Cs₂SnI₅Br₆   | 1.63  | 3.41    | 0.58    | 0.54 | 1.08 | FTO/bl-TiO₂/2% Sn-TiO₂/absorber/Cs₂SnI₅Br₆/HTM/LPAH/FTO | [226]|
| Cs₂SnBr₃     | 2.36  | 0.01    | 0.57    | 0.37 | 0.002 | FTO/bl-TiO₂/2% Sn-TiO₂/absorber/Cs₂SnBr₃/HTM/LPAH/FTO | [226]|
| Cs₂SnBr₄     | 2.85  | –       | –       | –   | –    | FTO/bl-TiO₂/2% Sn-TiO₂/absorber/Cs₂SnBr₄/HTM/LPAH/FTO | [226]|

consequence, it forms three short Ge–I bonds (2.73–2.77 Å) and three long in Ge–I bonds (3.26–3.58 Å). The Ge-based perovskites have been extensively studied by carrying computational work based on density functional theory (DFT). The size of constituent halide ion has a remarkable effect on the bandgap of Ge-based perovskites. The DFT calculations of bandgap values of CsGeX₃ [X-Cl, Br, I] showed the decreasing trend of 3.67, 2.32, and 1.53 eV, respectively. The small A-site cations + have two values of $V_{OC}$ that reported a SPCE of 0.57% as a light absorber in solar cells fabricated with planar p-i-n architecture having PEDOTS:PSS as HTM and PC₇₀BM as ETM. The mixed Ge-based perovskite RbSn₀.₅Ge₀.₅I₃ displays a 1D chain like perovskite structures are formed having indirect bandgaps. The introduction of bromide ions into MAGeI₃ perovskites enhances not only photovoltaic performance but also stability to a slight extent. The substitution of 10% of the iodide content by bromide results in MAGeI₂.₇Br₀.₃. The mixed Ge-based perovskite RbSn₀.₅Ge₀.₅I₃ displays a direct optical bandgap in the range of 0.9–1.6 eV with sufficient optical absorption spectrum comparable to MAPX₉ perovskites. The material exhibited favorable effective masses for higher carrier mobility and good stability in water. A 2D perovskite (Cs₂H₃(CH₂)₃NH₃)₂GeI₄ [(PEA)₂GeI₄] consisting of inorganic germanium iodide planes separated by organic PEAI layers has a direct bandgap of 2.12 eV that is very close to the value 2.17 eV obtained through DFT calculations. The perovskite material exhibits luminescence at room temperature with a medium lifetime and is a potential candidate for PV applications. The 2D (PEA)₂GeI₄ shows more stability in air than 3D MAGeI₃ that is attributed to the presence of a hydrophobic organic long chain. On the basis of DFT calculations, one more 2D Ruddlesden–Popper hybrid organic–inorganic perovskite Ba₂MA₃Sn₃I₁₀ [M = Sn or Ge, n = 2–4] has been reported that has suitable excitonic and optical light absorbing properties for application in lead-free perovskites. Moreover, 2D Ge-based perovskites have enhanced thermodynamic stability in comparison to their 3D counterparts that enables 2D Ge-based perovskites with a thickness of a few tens of unit cells to be used as light absorbers in perovskite solar cell. Table 8 shows some photovoltaic parameters of Ge-based perovskites. Figure 13 shows the crystal structure, band diagram, and the $I–V$ characteristics of Ge-based perovskites in a solar cell (a) CsGeI₃ and (b) MAGeI₃ (c) optical absorption spectrum of CsGeI₃, MAGeI₃, and FAGeI₃, in comparison with CsSnI₃, and (d) calculated band structure and projected density of states of CsGeI₃. The energy of the highest occupied state is set to 0 eV. (e) Photoelectron spectroscopy in air (PESA) of powder samples and (f) schematic energy level diagram of CsGeI₃, MAGeI₃, and FAGeI₃.

7.3. Bismuth-Based Perovskites

Bismuth can form $+$ ions with similar valence electronic configuration as that of Pb$^+$, having ionic radius (103 pm) in comparison to divalent Pb$^{2+}$ (119 pm) and Sn$^{2+}$ (110 pm). The value of electronegativity of bismuth is 2.02 in comparison to that of Pb (2.33) and Sn (1.96). Bismuth-based perovskites are represented with a general formula A₂Bi₂X₉, where A can be MA, Cs, NH₃, Ag. These materials have attracted large attention due to their low toxic nature. They can have 0D dimer, 1D chain like, 2D layered, or 3D double perovskite elpasolite frameworks containing A-site cations such as MA$^+$, Cs$^+$, Rb$^+$, K$^+$, guanidinium, cyclohexylammonium, imidazolium to form a 0D dimer perovskite structure. Bismuth-based methylammonium single crystal MABi₁₉ (MBI) shows a regular hexagon shape with a diameter ranging from 100 to 200 nm.
The MBI crystals exhibit a dark red color with an optical bandgap of \(\approx 2.11\) eV. The 0D MBI consists of face-sharing bi-octahedral \([\text{Bi}_2\text{I}_9]\) clusters surrounded by \(\text{MA}^+\) cations. The fabricated solar cells using MBI as light absorbing layer reported an efficiency of 0.08\% with \(J_{SC} \approx 0.36\) mA cm\(^{-2}\), \(V_{OC}\) of 0.51 V, and FF of 0.44. The photovoltaic performance was enhanced by using thick mesoporous TiO\(_2\) layer (1.8 \(\mu\)m) to \(V_{OC}\) of 0.51 V, \(J_{SC}\) of 1.16 mA cm\(^{-2}\), FF of 0.46, and SPCE of 0.19\%.\[127\]

| Light absorber | \(E_g\) | \(V_{OC}\) | \(J_{SC}\) | FF | SPCE | Architecture | Ref. |
|---------------|--------|------------|-----------|----|------|--------------|-----|
| MAGeI\(_3\)   | 2.0    | 0.15       | 4.0       | 0.30 | 0.2  | FTO/c-TiO\(_2\)/mp-TiO\(_2\)/absorber/Spiro-OMeTAD/Au | [144] |
| CsGeI\(_3\)   | 1.63   | 0.07       | 5.7       | 0.27 | 0.11 | FTO/c-TiO\(_2\)/mp-TiO\(_2\)/absorber/Spiro-OMeTAD/Au | [144] |
| CsGeI\(_3\)   | –      | 0.57       | 10.49     | 0.53 | 3.2  | FTO/mp-TiO\(_2\)/CsGeI\(_3\)/P3HT Au | [236] |

Table 8. Ge-based perovskites and their photovoltaic parameters.

Figure 13. Schematic diagram for the unit cell of a) CsGeI\(_3\) and b) MAGeI\(_3\); Reproduced with permission\[229\] Copyright 2015, American Chemical Society. c) Optical absorption spectrum of CsGeI\(_3\), MAGeI\(_3\), and FAGeI\(_3\), in comparison with CsSnI\(_3\). d) Calculated band structure and projected density of states of CsGeI\(_3\). The energy of the highest occupied state is set to 0 eV. e) Photoelectron spectroscopy in air (PESA) of powder samples and f) schematic energy level diagram of CsGeI\(_3\), MAGeI\(_3\), and FAGeI\(_3\); Reproduced with permission\[144\] Copyright 2012, Royal Society of Chemistry.
The positive Hall coefficient of MBI film reveals p-type charge carrier with carrier concentration of $10^{15}$–$10^{16}$ cm$^{-3}$ for solution-processed MBI films. MBI films have got excellent stability against exposure to humidity level of 50% and ambient air at room temperature for 40 d. The first study on bismuth-based perovskite (MA)$_3$Bi$_2$I$_9$ as a light absorber was reported by preparing simple (MA)$_3$Bi$_2$I$_9$ perovskite and mixed (MA)$_3$Bi$_2$I$_9$–Cl$_x$ perovskite thin films with a hexagonal crystaline phase. The mesostructured solar cells displayed a better SPCE of 0.12%, $V_{OC}$ of 0.68 V, $J_{SC}$ of 0.52 mA cm$^{-2}$, and FF of 0.33 as compared to (MA)$_3$Bi$_2$I$_9$–Cl$_x$ displaying SPCE of 0.003, $V_{OC}$ of 0.04 V, $J_{SC}$ of 0.18 mA cm$^{-3}$, and FF of 0.38. Also the substitution of iodine with chloride in (MA)$_3$Bi$_2$I$_9$ shifted the bandgap from 2.1 to 2.4 eV. An efficiency of 0.42% is achieved by using a mesoporous TiO$_2$ substrate for fabricating a (MA)$_3$Bi$_2$I$_9$ perovskite film with $V_{OC}$ of 0.67 V, $J_{SC}$ of 1.0 mA cm$^{-3}$, and FF of 0.62. The (MA)$_3$Bi$_2$I$_9$ films fabricated by evaporation-spin-coating process produced better quality films which produced SPCE of 0.39% in an inverted planar device with a $V_{OC}$ of 0.83 V, $J_{SC}$ of 1.39 mA cm$^{-2}$, and FF of 0.34. The gas-assisted deposition method enhances the morphology of active light absorber layer. The fabricated (MA)$_3$Bi$_2$I$_9$ light absorber layer by gas-assisted deposition process reported an enhanced value of SPCE of 0.08% and $V_{OC}$ of 0.686 V. The solvent annealing in (MA)$_3$Bi$_2$I$_9$ films enhances its electrical conductivity. The DFM-induced solvent annealing impacts the charge transport through the films. The morphology of (MA)$_3$Bi$_2$I$_9$ perovskite film can also be enhanced by incorporating a small amount of N-methyl-2 pyrrolidone (NMP) into the MBI-DMF solution. The addition of various concentration of active light absorber layer. The fabricated (MA)$_3$Bi$_2$I$_9$ light absorber layer by gas-assisted deposition process reported an enhanced value of SPCE of 0.08% and $V_{OC}$ of 0.686 V.[242] The solvent annealing in (MA)$_3$Bi$_2$I$_9$ films enhances its electrical conductivity. The DFM-induced solvent annealing impacts the charge transport through the films.[293] The morphology of (MA)$_3$Bi$_2$I$_9$ perovskite film can also be enhanced by incorporating a small amount of N-methyl-2 pyrrolidone (NMP) into the MBI-DMF solution. The addition of various concentration of MBI-DMF solution. The addition of various concentration of MBI-DMF solution. The addition of various concentration of MBI-DMF solution. The addition of various concentration of MBI-DMF solution. 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perovskite (MA)$_3$Bi$_2$I$_9$ has a bandgap of 2.00 V potential to be used as a lead-free perovskite material due to similar property as that of MAPbI$_3$ but Ti is toxic in nature. The bimetal iodide thin films AgBi$_2$I$_7$ show a SC of 1.22%, $V_{OC}$ of 0.56 V, $J_{SC}$ of 3.30 mA cm$^{-2}$, and FF of 1.87 with a better stability under ambient conditions. Using first principle calculations, a 3D double perovskite family has been revealed with optical bandstructure.

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of antimony-based perovskites used as light absorbers. In addition to it, the employed processing technique also affects the dimensions of the synthesized products. Cs$_3$Sb$_2$I$_9$ has an inclination to a 0D dimer form if it is prepared by solution process whereas it prefers a 3D layered structure when prepared through a solid-state or gas phase reaction. Saparov et al.[140] carried out thin film preparation and characterization of Cs$_3$Sb$_2$I$_9$ thin films as light absorber in perovskites solar cell. Cs$_3$Sb$_2$I$_9$ film exists in two forms, viz., a 0D dimer form and a 2D layered form. The 0D dimer form of Cs$_3$Sb$_2$I$_9$ is prepared through reactions of CsI and SbI$_3$ in stoichiometric ratio of 3:2 in polar solvents. This film has an intense orange color and is stable under ambient air with an indirect bandgap of 2.06 eV whereas 2D layered films of Cs$_3$Sb$_2$I$_9$ are obtained through a solid-state or gas phase reactions, that is, by sequential deposition of CsI film through evaporation followed by annealing in SbI$_3$ vapor. The layered films display red color with a direct bandgap of 2.05 eV, high absorption coefficient of $10^5$ cm$^{-1}$, and ionization energy of 5.6 eV with better stability in air. However, SPCE values of the perovskites solar device with layered forms of Cs$_3$Sb$_2$I$_9$ as light absorber have minimal values of SPCE close to 1% with $V_{OC}$ of 0.30 V and $J_{SC}$ below 0.1 mA cm$^{-2}$ indicating a very low overall photovoltaic performance attributed to the presence of deep defects that promote nonradiative recombination. Boopathi et al.[181] synthesized 0D dimer form of Cs$_3$Sb$_2$I$_9$ as a light absorber and reported a SPCE of 0.84%, $J_{SC}$ of 2.91 mA cm$^{-2}$, $V_{OC}$ of 0.60 V, and FF of 0.48 for Cs$_3$Sb$_2$I$_9$ with addition of HI.[181]

A 2D layered perovskite was synthesized by using the mixture Cs$^+$ and MA$^+$ as the A-site cation via solution process as opposed to reported by Saparov et al. where A-site cation is substituted by a smaller cation Rb$^+$. A 2D layered phase is achieved due to smaller radius of Rb$^+$ (1.72 Å) as compared to that of Cs$^+$ (1.88 Å) via solution processing through the reaction of Rbl and Sbl. Using DFT calculations, the comparison of formation energies of 2D layered and 1D dimer forms of A$_3$Sb$_2$I$_9$ (A-Cs, Rb) reveals that the formation energy difference of 0.25 eV is higher for Rb-based perovskites than that of cesium-based counterparts having this difference equal to 0.1 eV thus clearly indicating the increased inclination of Rb$_3$Sb$_2$I$_9$ for layered phase. The layered perovskites Rb$_3$Sb$_2$I$_9$ achieved a SPCE of 0.66% with $V_{OC}$ of 0.55 V, $J_{SC}$ of 2.11 mA cm$^{-2}$, and FF of 0.57.[267] In addition, they show thermal stability up to 250 °C and no phase transition is reported in between −40 and 200 °C. The light absorption coefficient of Rb$_3$Sb$_2$I$_9$ films is greater than $1 \times 10^5$ cm$^{-1}$ with an indirect bandgap of 2.1 eV. A direct transition at 2.24 eV was calculated for Rb$_3$Sb$_2$I$_9$ as compared to 2.05 eV for the bandgap of cesium. MA$_3$Sb$_2$I$_9$ only forms a 0D dimer structure. The octahedral anionic metal halide [Sb$_2$I$_9$]$^-$ surround the MA$^+$ cations. Hebig et al. first prepared the flat and thin films of MA$_3$Sb$_2$I$_9$ by spin-coating process followed by toluene treatment. The obtained thin films show a peak absorption coefficient above $10^5$ cm$^{-1}$ and an optical bandgap of 2.14 eV. The fabricated planar perovskite cell achieved SPCE of 0.49%, $V_{OC}$ of 0.90 V, $J_{SC}$ of 1.0 mA cm$^{-2}$, and FF of 0.55.[147] Boopathi et al.[181] synthesized 0D (MA)$_3$Sb$_2$I$_9$ films for use as light absorbers in perovskite solar cells with HI as an additive. The addition of HI into the films resulted in an increase in light absorption in the visible wavelength regions about 400 nm. The XRD spectra studies revealed that the addition of HI leads to a better crystallinity, phase purity, and quality of the film. It reduces the bandgap thereby enhancing the light absorption.
absorption toward higher wavelength regions. The achieved values of photovoltaic parameters with or without addition of HI are shown in Table 9. The nonsolvent treatment was investigated to enhance the surface morphology of Sn-based dimer by using HI-CB to enhance the heterogenous nucleation of Sb-based perovskite used as light absorber.[268] The interlayer of HI-CB acted as a hydrophobic scaffold for the growth of (CH3NH3)2SbI3 crystals. The interlayer decreases the number of voids and enhances the quality of film. The fabricated films achieved a SPCE of 2.77%.[268] The DFT calculations have revealed that the most stable mixed metal organic–inorganic perovskite MA2SbI6 has a bandgap of 2.0 eV which is further confirmed by using XRD characterization of MA2SbI6 as a light absorber that has displayed an optical bandgap of 1.93 eV and good stability in air.[269]

A larger A-site cation was used to synthesize high-quality films of 2D layered phase (CH3NH3)2SbClI6- x. The induction of methylammonium chloride into precursor solutions inhibits the formation of the undesirable 0D dimer phase leading to synthesis of high-quality films of 2D layered phase that is favorable for application in lead-free perovskite solar cells. These films achieved a SPCE of 2%.[270] Similarly, Zuo and Ding synthesized a family of perovskite light absorbers (NH4)3(Sb1-xBix)2I9 as light absorber for perovskite solar cells.[271] The A-site resulting in a switch of current direction on illumination.[272] The directions of dark and photocurrent densities were opposite.[273] The fabricated MASbSI2 as light absorber achieved SPCE of 3% under the standard illumination.

ASbBr2 is a black crystalline solid with an optical bandgap of 1.65 V that is much lower than that of conventional MAPbBr3 of 2.3 eV. The planar cells with standard architecture using P3HT as a HTM layer displayed better photovoltaic parameters as JSC (5.1 mA cm-2), VOC (1.285 V), FF (0.58), and SPCE of 3.8% whereas the inverted architecture using a double-layer PDI as ETL films is fabricated by depositing first by spin-coating from chlorobenzene solution followed by evaporation of additional layers of the material in vacuum and has shown JSC of 5.1 mA cm-2, VOC of 1.030 V, FF of 0.58, and SPCE of 3.1% only.[274] The effect of substitution of antimony (Sb) with bismuth (Bi) in a 2D mixed layered perovskite (NH4)3(Sb1-xBix)I9 as light absorber has been investigated extensively. The partial substitution of Sb with Bi did not change the structure of the crystal but enhanced the volume of the unit cell. The XRD patterns did not show any impurity phase with Bi addition but peaks shift toward lower angles as content of Bi increases showing an increase in unit cell size due to induction of bulkier bismuth cation. The films showed typical features of direct bandgaps due to strong absorption above 2.7 eV and indirect bandgaps because of absence of photoluminescence with long carrier lifetimes. The absorption coefficient increases due to increase in density of states in conduction band whereas bandgap reduces from 2.27 to 2.16 eV[275] for 5% Bi film due to higher spin–orbit coupling. Bismuth pushes the conduction band downward as predicted by DFT calculations. It also shifts the valence band downward, thereby enhancing the ionization potential values from 5.78 to 5.9 eV for incorporation of 50% bismuth content. The Urbach energies also showed a decrease with an increase in bismuth content. The carrier lifetimes do not follow a particular trend with increase in Bi incorporation in the perovskite film as 184 ± 8 ns (0% Bi), 94 ± 25 ns (20%Bi), 149 ± 12 ns (40% Bi), 91 ± 13 ns (50% Bi) as there is decrease in deep defects near the conduction band side due to addition of Bi but simultaneously there is an increase in defects near the valence band. The AC Hall measurements predicted the p-type conduction band behavior for (NH4)3SbI4 with a carrier concentration of 3.95 × 1015 cm-3 and mobility of 0.5 ± 0.5 cm2 V-1 s-1. The carrier density is reduced by incorporating 10 and 20% of Bi owing to increase in mobility that got doubled to more than 1 cm2 V-1 s-1 thus the material undergoes a p-to-n transition for higher Bi contents (40%, 50%) that clearly indicates the changing nature of defects in the material. Therefore, the films show both p and n-type regions. In order to increase p and n regions, electrical poling was used to adjust the load composition of the film by creating ionic drift. The unpoled (NH4)3SbI9 (p-type) showed linear photocurrent voltage relationship. The device was negatively poled by applying a bias of –2 V μm-1 to electrode B under illumination by a blue LED (455 nm, power 1.4 mW mm-2) for 2 min.[275] The V–I curves after negative poling indicates photovoltaic effect with VOC close to 200 mV which flipped to −0.2 V on ± poling.[275] The material exhibited measurable photocurrent densities at short-circuit conditions. The directions of dark and photocurrent densities were opposite resulting in a switch of current direction on illumination due to presence of opposite fields in the same compound. A negative voltage close to −0.6 V is required to achieve zero current condition in dark as opposed to +0.2 V required under illumination. Table 10 shows some photovoltaic parameters of...
antimony-based lead-free perovskites. The device configuration is shown in Figure 15 for the switchable photovoltaic device containing (NH₄)₂(Sb₁₋ₓBiₓ)I₉ perovskite material.[275]

### 7.5. Copper-Based Perovskites

The divalent Cu²⁺ cation is another suitable element for Pb²⁺ substitution as Cu⁺⁺ has nontoxic nature. Cu²⁺ has a small ionic radius (73 pm) as compared to Pb²⁺ (119 pm) and Sn²⁺ (110 pm). The divalent Cu²⁺ is more stable in air than Sn²⁺ and Ge²⁺.[135,136] Cu-based perovskites usually form 2D layered perovskite structures owing to their smaller ionic radii with general formula (RNH₃)₂CuX₄ where RNH₃ can be aliphatic or aromatic cation and X is a halogen. They can be easily prepared under suitable conditions by solution method. A 2D cupric perovskite solar cell [p-F-C₆H₅C₂H₄-NH₃]₂CuBr₄ and (CH₃(CH₂)₃NH₃)₂-CuBr₄ with absorption range from 300 to 750 nm has been reported. The achieved SPCE values of the fabricated perovskite solar cell are 0.51 and 0.63%, respectively, with good air stability of less than 5% decrease of efficiencies after 1 d in air with humidity of 50% without encapsulation. The reported photovoltaic parameters of the fabricated device are shown in Table 10.[135] The solar cells based on MA₂CuCl₂Br₂ have been investigated in order to study the photovoltaic performance and stability of Cu-based mixed halides. By tuning Cl/Br ratio, the optical absorption can be extended in the near-infrared region. The small quantity of Cl⁻ enhances the stability and crystallization of the perovskite material. Among all the investigated light absorbers, the highest SPCE of 0.17% is achieved using MA₂CuCl₂Br₂ as light absorber. The minimal values of SPCE are attributed to reduction of Cu²⁺ and low absorption coefficient. The formation of Cu²⁺ ions was found to be responsible for the green photoluminescence of this material. (MA)₂CuCl₂Br₂ and (MA)₂CuCl₀.₅Br₃.₅ are found to be more stable under ambient conditions. The achieved values of photovoltaic parameters are shown in Table 10.[136] It has been found that adding a small amount of CuBr₂ into MAPbI₃ remarkably enhances its morphology and efficiency but it is still under investigation whether Cu²⁺ can actually act as substituent for Pb²⁺.[276]

Li et al. investigated and characterized highly stable Cu-based perovskite films C₆H₄NH₂CuBr-I exhibiting extraordinary hydrophobic behavior with a contact angle of ≈90°. The XRD patterns of the perovskite films did not report any change even after 4 h of being immersed in water. The UV absorption of these films revealed their excellent absorption over the entire visible spectrum with low values of SPCE of ≈0.5% attributed to low absorption coefficient and heavy mass of holes.[117] The other Cu-based perovskite solar cells (CH₃NH₃)₂CuCl₄ and (CH₃NH₃)₂CuCl₂X₂ [X = I, Br] were fabricated through grinding milling process by Elseman and team and on characterization by XRD reveals that (CH₃NH₃)₂CuCl₄ has monoclinic crystal structure and (CH₃NH₃)₂CuCl₂Br₂ is crystallized with an orthorhombic structure. The tolerance factor and octahedral factor calculated for (CH₃NH₃)₂CuCl₄ were found to be 1.004 and 0.403, respectively, by assuming the ionic radius of methylammonium to be 18 pm. The calculated values are out of the optimum range of 0.8 < t < 0.9 and 0.42 < u < 0.895 for a stable 3D

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**Table 10. Antimony-based lead-free perovskites used as light absorber.**

| Light absorber | E_g  | J_SC | V_OC | FF  | SPCE | Architecture | Ref.       |
|---------------|------|------|------|-----|------|--------------|------------|
| Cs₅Sb₂I₉      | 2.05 | <0.1 | 0.31 | –   | <1.0 | FTO/C-TiO₂/absorber/PTAA/Au | [140]     |
| Cs₅Sb₂Br₅     | 2.30 | 2.34 | 0.62 | 0.46| 0.67 | ITO/PEDOT:PSS/absorber/PC₆₁BM/C₆₀B/C/BP/Al | [181]     |
| Cs₅Sb₂I₉+HI   | 2.0  | 2.91 | 0.60 | 0.48| 0.84 | ITO/PEDOT:PSS/absorber/PC₆₁BM/C₆₀B/C/BP/Al | [181]     |
| Rb₂Sb₂I₉      | 2.1  | 2.11 | 0.55 | 0.57| 0.66 | FTO/C-TiO₂/mp-TiO₂/absorber/PolypT/P/Au | [267]     |
| MA₃Sb₂I₉      | 2.14 | 1.0  | 0.90 | 0.55| 0.49 | ITO/PEDOT:PSS/absorber/PC₆₁BM/nano-ZnO/Au | [147]     |
| MA₃Sb₂I₉      | 2.20 | 3.81 | 0.64 | 0.45| 1.11 | ITO/PEDOT:PSS/absorber/PC₆₁BM/C₆₀B/C/BP/Al | [181]     |
| MA₃Sb₂I₉+HI   | 1.95 | 5.41 | 0.62 | 0.60| 2.04 | ITO/PEDOT:PSS/absorber/PC₆₁BM/CO₆₀B/C/BP/Al | [181]     |
| (NH₄)₂Sb₂IXBr₉ | 2.27 | 1.15 | 1.03 | 0.42| 0.51 | ITO/PEDOT:PSS/absorber/PC₆₁BM/Al | [116]     |
| MASbSI₂       | 2.03 | 8.12 | 0.65 | 0.58| 3.08 | FTO/mp-CrO₂/absorber/P3HT/P3TF/PEDOT:PSS/Au | [271]     |
| Cs₅CuSb₂Cl₄   | 1.0  | –   | –   | –   | 0.30 | –            | [272]     |
| (N-EtPY)SbBr₄ (standard) | 1.65 | 5.1  | 1.285 | 0.58| 3.8  | ITO/C-TiO₂/absorber/P3HT/Au | [274]     |
| (N-EtPY)SbBr₄ (inverted) | 1.65 | 5.1  | 1.030 | 0.58| 3.1  | ITO/PEDOT:PSS/absorber/P1D1/Ag | [274]     |
| CH₃Sc(NH₂)₂Sb₂A₃ | 2.41–3.34 | – | – | – | – | – | [275] |
perovskite structure thus it crystallizes into 2D structures.[277]
It has been observed that the substitution of Cl\(^-\) with I\(^-\) or Br\(^-\) has different effects on bond angles, unit cell dimensions, and ionic radius. The achieved photovoltaic parameters are depicted in Table 11. The low SPCE values of (CH\(_3\)NH\(_3\))\(_2\)CuCl\(_2\)Br\(_2\) are due to reduction of Cu\(^{2+}\) caused by the higher trap density. The chemical structures and the performance of Cu-based perovskite solar cells (a) (CH\(_3\)NH\(_3\))\(_2\)CuCl\(_4\), (b) (CH\(_3\)NH\(_3\))\(_2\)CuCl\(_2\)I\(_2\), and (c) (CH\(_3\)NH\(_3\))\(_2\)CuCl\(_2\)Br\(_2\) powders, (d) current–voltage curve, and (e) EQE spectra of solar cells are shown in Figure 16.[277]

### Table 11. Photovoltaic parameters of reported Cu-based perovskites.

| Light absorber | \(J_{SC}\) [mA cm\(^{-2}\)] | \(V_{OC}\) | PCE | FF | \(E_g\) | Architecture | Ref. |
|----------------|-------------------------------|-----------|-----|----|----------|--------------|------|
| (CH\(_3\))(CH\(_2\))\(_3\)NH\(_3\))\(_2\)CuBr\(_4\) | 1.78 | 0.88 | 0.63 | 0.40 | 1.76 | FTO/C-TiO\(_2\)/mp-TiO\(_2\)/absorber/Spiro-OMeTAD/Ag | [135] |
| (p-F-C\(_6\)H\(_5\)C\(_2\)H\(_4\))-NH\(_3\))\(_2\)CuBr\(_4\) | 1.46 | 0.87 | 0.51 | 0.40 | 1.74 | FTO/TiO\(_2\)/absorber/Spiro-OMeTAD/LiTFSI/Ag | [135] |
| MA\(_2\)CuCl\(_2\)Br\(_2\) | 0.22 | 0.26 | 0.02 | 0.32 | 2.12 | FTO/C-TiO\(_2\)/mp-TiO\(_2\)/absorber/Spiro-OMeTAD/Au | [136] |
| MA\(_2\)CuCl\(_3\)Br\(_2\) | 0.21 | 0.29 | 0.002 | 0.28 | 1.8 | FTO/C-TiO\(_2\)/mp-TiO\(_2\)/absorber/Spiro-OMeTAD/Au | [136] |
| C\(_6\)H\(_4\)NH\(_2\)CuBr\(_2\)I | 6.20 | 0.20 | 0.46 | 0.46 | 1.64 | FTO/C-TiO\(_2\)/mp-TiO\(_2\)/absorber/ZrO\(_2\)/Cu | [137] |
| (CH\(_3\)NH\(_3\))\(_2\)CuCl\(_4\) | 8.12 | 0.56 | 2.41 | 0.52 | 2.36 | Glass/FTO/TiO\(_2\)/absorber/Spiro-OMeTAD/Au | [277] |
| (CH\(_3\)NH\(_3\))\(_2\)CuCl\(_2\)I\(_2\) | 6.78 | 0.54 | 1.75 | 0.47 | 1.90 | Glass/FTO/TiO\(_2\)/absorber/Spiro-OMeTAD/Au | [277] |
| (CH\(_3\)NH\(_3\))\(_2\)CuCl\(_2\)Br\(_2\) | 3.35 | 0.58 | 0.99 | 0.50 | 1.04 | Glass/FTO/TiO\(_2\)/absorber/Spiro-OMeTAD/Au | [277] |

7.6. Other Potential Candidates for Lead-Free Perovskites

The alkaline earth metals Be\(^{2+}\), Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), and Ba\(^{2+}\) have been investigated as an alternative to lead in lead-free perovskite. However, the optical bandgap of Be\(^{2+}\) is too high to be used for PV applications. Mg\(^{2+}\) despite having a smaller ionic radius (72 pm) can replace Pb\(^{2+}\) (119 pm) to form a stable magnesium-based perovskite.[278,279] The replacement of Pb\(^{2+}\) by Mg\(^{2+}\) results in a lead-free magnesium-based AMgX\(_3\) perovskite that exhibits low effective masses, direct optical absorption coefficients, and direct bandgap tunable within the visible region of electromagnetic spectrum depending upon the size of A-site cation.[278,279] The bandgaps of magnesium-based perovskite AMgI\(_3\) featured an increasing trend with A-site cations such as FA\(^+\), MA\(^+\), and Cs\(^+\) having values 0.9, 1.5, and 1.7 eV, respectively.[278] The study of photoluminescence properties of Eu\(^{2+}\)-doped CsMI\(_3\) [M=Mg, Ca, Sr] perovskite has revealed that the Eu\(^{2+}\)-doped CsMgI\(_3\) and CsSrI\(_3\) displayed a redshift emission with respect to Eu\(^{2+}\)-doped CsCaI\(_3\) perovskite. Eu\(^{2+}\)-doped CsMgI\(_3\) crystallizes in a distorted hexagonal CsNiCl\(_3\) structure.
whereas CsCaI$_3$ crystallizes in an orthorhombic GdFeO$_3$ structure and CsSrI$_3$ crystallizes in a filled PuBr$_3$ structure.[286]

The divalent Ca$^{2+}$ has an ionic radius (100 pm) comparable to that of Pb$^{2+}$ (119 pm)[281,282] whereas Sr$^{2+}$ (118 pm) has a similar ionic radii to Pb$^{2+}$ (119 pm).[283] The divalent Ba$^{2+}$ has an ionic radii of 135 pm larger than that of Pb$^{2+}$ (119 pm).[283] The DFT calculations have reported bandgaps of MACaI$_3$, MASrI$_3$, and MASrI$_3$ and MABaI$_3$ do have large bandgaps leading to light reaching 0.85.[284] Transition metals such as Ti, V, Mn, Ni, Pd, increase in long carrier lifetime and fill factors of the devices sized through low-temperature solid-state reactions.[290] The size of halide anion has a direct effect on the canted spin.[288]

The optical properties of gold-based 2D organic mixed AuI/AuIII structure of bis(alkyl ammonium)metal(II) tetrahalide ($\text{[NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3\text{]}^2$ $\text{[Au I I 2]}$ $\text{[Au III I 4]}$($\text{I}_3$)$^2$ and $\text{[NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3\text{]}^2$ $\text{[Au I I 2]}$ $\text{[Au III I 4]}$($\text{I}_3$)$^2$ has been investigated for its potential in a perovskite framework.[285] The BaZrS$_3$ exhibited a distorted perovskite structure and bandgap of 1.9 eV.[286] The divalent rare earth Eu$^{2+}$ and Sr$^{2+}$ in Cs$_2$TiBr$_6$ have been prepared through low-temperature solid-state reactions. [287] The DFT simulations of mixed chalcogen perovskite with chalcogen and halogen anions have not been possible due to their unstable nature.[289] The divalent Ca$^{2+}$ and Sr$^{2+}$ in MAPbI$_3$ perovskite thin films has reported an increase in long carrier lifetime and fill factors of the devices reaching 0.85.[284] Transition metals such as Ti, V, Mn, Ni, Pd, Fe, Cu, Zn, Cd, and Hg have been researched extensively for lead replacement in lead-free perovskite. The crystals of CsNIX$_3$ perovskite have been synthesized by hydrothermal method having BaNiO$_3$ structure consisting of a face-sharing NiX$_6$ octahedral separated by CsX$_{12}$ cuboctahedra.[285] The 2D layered perovskite structure of bis(alkyl ammonium)metal(II) tetrahalide ($\text{[C}_6\text{H}_{12}\text{O},\text{NH}_3\text{I}_2]\text{MX}_4$ and ($\alpha\text{w}$) polymethylene diammonium metal (II) tetrahalide $\text{NH}_4\text{CH}_3\text{I}_3\text{NH}_4\text{MX}_4$ with $\text{M}=$Ca, Cu, Fe, Mn, or Pd and X=Br, Cl have been synthesized and a large single perovskite crystal has been obtained.[286] The divalent Fe$^{2+}$ has a smaller ionic radius (78 pm) as compared to Pb$^{2+}$ (119 pm) that does not allow the formation of 3D perovskite structure. Iron-based 2D layered perovskite ($\text{CH}_3\text{NH}_3\text{I}_3\text{FeCl}_4$) exhibits a canted anti-ferromagnetism in a magnetic field of strength greater than 2000 Oe and it also exhibits the phase transition from a high symmetry to a low symmetry.[287] The magnetic susceptibility of ($\text{CH}_3\text{NH}_3\text{I}_3\text{FeCl}_4$)Br perovskite depends upon the strength of applied magnetic field. Also, the size of halide anion has a direct effect on the canted spin.[288] Just like Sn-based perovskite, iron-based perovskite is also unstable due to oxidation of Fe$^{2+}$ to Fe$^{3+}$.[289] The divalent rare earth Eu$^{2+}$-based perovskite ($\text{C}_6\text{H}_{12}\text{O},\text{NH}_3\text{I}_2]$ $\text{FeCl}_4$) has been synthesized through low-temperature solid-state reactions.[290] The effect of doping of rare earth metal ions such as Eu$^{2+}$, Tm$^{3+}$, and Yb$^{2+}$ in Cs$_3\text{AX}$($\text{A}=$Ca, Mg, Sr) perovskite has been investigated extensively.[280,291,292] Another transition metal gold has been investigated for its potential in a perovskite framework. The optical properties of gold-based 2D organic mixed AuI/AuIII layered perovskite have been reported with $\text{[AuI}_3]/[\text{AuIII}_2]$ layers supported by I$^{-}$ ions and appropriate organic dications.[293] The [NH$_4$(CH$_3$)$_3$I]$_2$ [AuI$_3$] [AuIII$_2$]($\text{[I}_2$$_3$]$_2$ and [NH$_4$(CH$_3$)$_3$I]$_2$ [AuI$_3$] [AuIII$_2$]($\text{[I}_2$$_3$]$_2$ perovskite exhibited a bandgap of 0.95 and 1.14 eV, respectively. The low bandgaps are attributed to the induced electronic interactions between [AuI$_3$]$_2$ and [AuIII$_2$]$_2$ units and I$_2$$_3$ units.[293] Another transition metal tellurium-based vacancy order perovskite Cs$_5$TeI$_6$ has been reported that consists of a face-centered lattice of [TeI$_4$]$^{3-}$ units with Cs$^{2+}$ cations occupying the cuboctahedral position. This material do possess an indirect bandgap, electronic dispersion, and is intolerant to formation of defects that is not suitable for PV applications as per current research.[294] Transition metal titanium-based perovskite thin films Cs$_5$TiBr$_6$ have been prepared through low-temperature-based method having a bandgap of 1.8 eV that is comparable to eV of lead halide perovskite, balanced carrier diffusion lengths > 100 nm, and highly stable under environmental stresses. The fabricated device exhibited a SPCE of 3.3%. The incorporation of C$_{60}$ interfacial layer between the Cs$_5$TiBr$_6$ light absorber thin films and TiO$_2$ ETM resulted in a $V_{oc}$ of 1.02 V in a reverse scan direction and also enhanced other photovoltaic parameters. The thin films are highly stable under ambient conditions.[294] By the application of split anion approach to replace MAPbI$_3$, the replacement of Pb$^{2+}$ with Bi$^{3+}$ and I$^{-}$ with Se$^{-}$ or S$^{-}$ is done to maintain the charge neutrality thus resulting in lead-free perovskite CH$_3$NH$_3$BiSe$_2$I$_3$ and CH$_3$NH$_3$BeS$_2$I$_3$ has been reported exhibiting a direct bandgap of 1.3–1.4 eV suitable for photovoltaic applications.[295] Figure 17 shows the atomic structure and bandgap diagram of CH$_3$NH$_3$PbI$_3$ and MABISeI$_2$ and a schematic illustrating the split-anion approach to replace Pb in CH$_3$NH$_3$PbI$_3$.[295]

Lead-free perovskite with mixed chalcogen and halogen anion AB(CH$_3$,X)$_3$ where A: Ca or Ba, B: Sb or Bi, X: halogen, Ch: chalcogen has been investigated by using DFT calculations and solid-state reactions that revealed their thermodynamically unstable nature, that is, their liability to decompose into ternary or binary secondary phases or form phases with nonperovskite structure. The synthesis of mixed perovskite with chalcogen and halogen anions has not been possible due to their unstable nature.[289] The bandgaps of chalcogenide perovskite CaTi$_3$, BaZrS$_3$, CaZrSe$_3$, and CaHfSe$_1$ with a distorted structure are within the suitable range for photovoltaic performance. Due to their suitable optical absorption properties, chalcogenide perovskite can be the potential candidates to combat the instability and toxicity issues.[296] The synthesis of polycrystalline chalcogenide perovskite BaZrO$_3$, CdZrO$_3$, SrTiS$_3$, SrZrS$_3$, and BaSrZrO$_3$ has been reported by sulfonation of oxide perovskite by Cs$_2$S. The BaZrS$_3$ exhibited a distorted perovskite structure as evident from XRD pattern, with an optical absorption from UV to visible region. The perovskite material displayed photoluminescence in visible region and has an excellent stability in ambient air as compared to lead-based halide perovskites.[286] The quaternary halide double perovskite employing lanthanides (La$^{3+}$, Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Dy$^{3+}$, Er$^{3+}$, Tm$^{3+}$, Lu$^{3+}$) and actinides (Pu$^{3+}$, Am$^{3+}$, Bk$^{3+}$) has been investigated but no PV performance has been reported.[289,300] Table 12 summarizes the stability of lead-free perovskites.

8. Recent Research on Lead-Free Perovskites

In order to explore the potential material whose properties can be tailored to be used as a light absorber in a perovskite solar cell, a lot of research is being carried out at present. Research is going on to explore a perovskite material that is lead-free, nontoxic, have low fabrication cost, easy fabrication technique, higher SPCE, and better stability in air, moisture, and heat. In an attempt to synthesize a low-cost lead-free perovskite solar cell, the CH$_3$NH$_3$SnBr$_{3-x}$$_{x}$ crystals with a trigonal phase have been synthesized via aqueous solution based method by a reaction between HCl and H$_3$PO$_2$ without taking into account any protection against moisture. The synthesized crystals exhibit various low-frequency vibrational modes of Sn--Cl and Sn--Br.[281] Recent studies of lead-free perovskite have shown that the hot antisolvent treatment of perovskite film increases its coverage and inhibits electrical shunting in photovoltaic device. Also, the average crystallite size increases due to
annealing under a low partial pressure of dimethyl sulfoxide vapor. The topographical and electrical qualities of the perovskite film are enhanced facilitating the fabrication of tin-based perovskite solar cell with a SPCE of over 7%. The effect of additives on the stability of lead-free CsSnI₃ perovskite films has been studied by using first principle based calculations. It has been reported that the additives effectively passivate the surface and enhance the stability of CsSnI₃ films. The addition of SnBr₂ as an additive in CsSnI₃ films resulted in a SPCE of 4.3% with 100 h of stability.

An additional additive formamidinium thiocyanate into quasi-2D tin perovskite suppresses the oxidation of the material during film formation resulting in a highly crystalline structure with a coarser perovskite grain. The fabricated tin-based perovskite solar cell reported a SPCE of 8.17% under a reverse scan and a steady-state efficiency of 7.84%. The fabricated device retained 90% of its efficiency after 1000 h in a glove box filled with nitrogen. Another study on mixed tin-germanium perovskite solar cell FA₀.₇₅MA₀.₂₅Sn₁₋ₓGeₓI₃ has reported that most of the Ge atoms passivate the graded structure of tin perovskite. Upon doping with 5 wt% of Ge, the reported \( J_{SC} \) (19.8 mA cm⁻²), FF (0.55), and SPCE (4.48%) have shown an increasing trend as compared to 0 wt% of Ge. On further increasing the doping of Ge, the photovoltaic parameters have shown a decreasing trend. The doping of Ge also enhances the stability in air as compared to the nondoped sample.

A recent research on Mn and Ni-doped CsGeI₃ perovskite has revealed the effect of doping of Mn and Ni in CsGeI₃ perovskite that has resulted in enhancement of optical absorption and photoconductivity in visible and UV light region. The optical absorption, dielectric constant, and photoconductivity of Mn-doped CsGeI₃ perovskite are larger than that of Ni-doped counterpart. The Mn-doped CsGeI₃-MnCl₃ perovskite exhibited the potential properties that make it best among all the inorganic pure and metal-doped CsGeI₃ perovskite.

Figure 18 shows the light absorption spectrum of pristine and metal-doped (Ni, Mn) CsGeI₃ perovskite as a function of: (a) photon-energy-dependent absorption coefficient, (b) wavelength-dependent absorption coefficient, (c) reflectivity, (d) conductivity, (e) dielectric constant (real part), and (f) dielectric constant (imaginary part). In a recent study, lead-free bismuth-based perovskite CH₃NH₃BiX₃ (X3-I2Te, I2S, I2Se) as a light absorber has been investigated by using first principle calculations. The study has...
Table 12. Stability of lead-free perovskites.

| Light absorber | SPCE | Stability | Ref. |
|----------------|------|-----------|------|
| MAsnI3+SnF2    | 2.14%| 200 h under 1 sun degradation conditions (AM 1.5, 100 mW cm⁻²) | [194] |
| (FA)0.75(MA)0.25SnI3 | 8.12%| ≈80% of SPCE over a period of 400 h, stored in a glove box filled with nitrogen | [150] |
| MASnBr3.3Cl0.2 | 3.1% | Average lifetime less than 100 ps | [191] |
| FASnI1         | 6.23%| Stable efficiency of 6% for more than 100 s | [172] |
| en[FSnI3]      | 7.14%| Unencapsulated device continues to have 96% of initial SPCE after 1000 h | [208] |
| (PEA)2(FA)8Sn9I28 | 5.94%| Unencapsulated devices display performance without significant decay in SPCE over 100 h | [156] |
| FASnI3 +EDAI2 (1%) | 7.4% | Device stored in glove box displays maximum SPCE of 8.9% for over 1400 h with only slight reduction for storage beyond 2000 h | [203] |
| FASnI3         | 5.5% | Encapsulated devices exhibit stability over 1000 h under continuous 1 sun illumination encompassing UV region | [167] |
| CsSnIBr2+HPA   | 3%   | Exhibits stable efficiency for 77 d and power output within 9 h at high temperature up to 473 K | [193] |
| (PEA)2CeI6    | –    | 2D structure is more stable than 3D MAGeI3 in air. | [234] |
| BA3MA2−xMnI3+x+1 | 1.94–2.53%| 2D structure is more stable as compared to 3D counterparts. | [235] |
| MA3BiI3       | 0.356%| Exhibits air and moisture stability for more than 60 d | [264] |
| MA3BiI3 + NMP | 0.31%| Unencapsulated device exhibits 88% of SPCE to relative 50–60% humidity for 30 d | [244] |
| MA3BiI3       | 0.26%| Exhibits stability for more than ten weeks under ambient conditions | [174] |
| Cs3BiI5       | 8%   | Unencapsulated device displays initial SPCE for more than 500 h under 1 sun at 65 °C and relative humidity of 60–70% | [141] |
| MA3BiI3 (with FPDI ETM) | 0.06%| Exhibits limited degradation in SPCE after 17 d storage in ambient atmosphere | [245] |
| MA3BiI3       | 0.17%| Exhibits 56% of peak SPCE after 300 h exposure to air | [262] |
| Cs3AgBiBr6    | 2.43%| Unencapsulated device displays excellent stability to working conditions. | [266] |
| AgBiI3        | 1.22%| Exhibits excellent stability for at least 10 d under ambient conditions | [265] |
| Cs3AgBiBr6    | –    | Degrades after light exposure for two weeks | [265] |
| KBI3 H2O      | –    | Exhibits considerable stability in air | [252] |
| Cs3BiAgBr6    | –    | Exhibits stable SPCE in ambient conditions | [254] |
| Cs3AgBiBr6    | –    | Exhibits degradation after a period of three weeks on exposure to ambient air and light | [256] |
| MA3BiI3 via (VASP) | 3.17%| Unencapsulated devices display stability for 60 d with 0.1% loss in SPCE | [247] |
| Cs3SbI4       | <1.00%| Increased stability under ambient air in comparison to MAPbI3 films stored in same condition | [140] |
| MA3BiI3       | –    | Exhibits stability at room temperature in air with 20–60% humidity for 370 d | [269] |
| MA3BiI3       | 0.12%| Exhibits no degradation over a month in devices stored in dark in dry air with humidity less than 10% | [111] |
| Cs3BiI3       | 1.09%| Unencapsulated devices exhibited SPCE decreasing at a slow pace, 75% of efficiency even after weeks of storage in a N2 filled glove box under ambient light | [186] |
| AgBiI3<sub>x</sub> | 0.60%| Unencapsulated devices displayed 94% of SPCE after 14 d at 70 °C, 30% RH and ambient light illumination retained 85% of efficiency | [294] |

1 < x < 2.25 (Ag4Bi7I25)
confirmed that CH$_3$NH$_3$BiX$_3$ (X = I$_2$Te, I$_2$S, I$_2$Se) perovskites are nontoxic in nature exhibiting a high optical absorption in the visible region. These properties pave the way for use of such bismuth-based perovskites as a light absorber as an alternative to lead-based CH$_3$NH$_3$PbI$_3$ perovskite in photovoltaic applications.[306] In another study, lead-free mixed chalcogen halide perovskite material MABiI$_2$S have been synthesized and characterized for its physical and optical properties that revealed a low bandgap of 1.52 eV suitable for optical absorption in the visible spectrum. The fabricated material exhibited an absorption up to over 1000 nm.[307] The concentration of perovskite solution (0.15–0.30 m) has an effect on the crystallization in MA$_3$Bi$_2$I$_9$ films. Also, the speed of rotation during spin-coating process determines the layer coverage. The SPCE of the fabricated cells enhances from 0.004 to 0.17% after processing. The fabricated device has exhibited a $V_{OC}$ of 0.72 V after 48 h.[308] Lead-free inorganic AgBiI$_4$ as a light absorber has been prepared by solution method of thin films. The AgBiI$_4$ films have been fabricated by 0.6 m solution and annealed at 150 °C. The films exhibited a better morphology with a thermal stability and photo-stability than that of MAPbI$_3$. The fabricated PSC exhibited 2.1% efficiency. The devices displayed long-term stability and maintained 96% of initial SPCE even after 100 h at relative humidity of 26%. Lead-free copper halide perovskite Cs$_3$Cu$_2$I$_5$ have

| Light absorber     | SPCE | Stability                                      | Ref.   |
|--------------------|------|------------------------------------------------|--------|
| RbSn$_0.5$Ge$_0.5$I$_3$ | –    | The activation barrier for water penetration is 0.23 eV in a humid environment that is much higher than for MAPbI$_3$ (0.09 eV). | [233]  |
| CsGeI$_3$          | 0.11%| Stable up to 350 °C                             | [144]  |
| MAGeI$_3$          | 0.20%| Stable up to 250 °C                             |        |
| FAGeI$_3$          |      | Stable up to 250 °C                             |        |
| MA$_3$Ni$_2$I$_5$  | 5.8% | Continuous to have 80% of initial SPCE in first 12 h in a properly sealed nitrogen glove box | [106]  |
| MA$_3$Bi$_2$I$_9$  | 0.19%| Films display stability over 40 d on conditional exposure to 50% humidity level at room temperature | [127]  |
| (NH$_4$)$_3$Sb$_2$I$_9$ | 0.51%| Films retained 80% of initial SPCE when stored in a glove box with O$_2$ < 10 ppm and H$_2$O < 0.1 ppm for 40 d but when in air with 50% humidity, the films lost their PV performance completely | [116]  |

**Table 12.** Continued.

Figure 18. Light absorption spectrum of pristine and metal-doped (Ni, Mn) CsGeI$_3$ perovskite as a function of a) photon energy dependent absorption coefficient, b) wavelength-dependent absorption coefficient, c) reflectivity, d) conductivity, e) dielectric constant (real part), and f) dielectric constant (imaginary part). Reproduced with permission.[305] Copyright 2018, Royal Society of Chemistry.
been reported with a 0D structure exhibiting a blue emission (>445 nm) with a high quantum yield of 90 and 60% for single crystals and thin films. The 0D electronic nature of Cs2CuI3 is attributed to a large exciton binding energy of 49 meV and blue emission is demonstrated using solution method Cs2CuI3 thin films.[310] Zinc-based lead-free CsZnCl3I perovskite 3D thin films have been reported that were deposited at 100 °C by aerosol-assisted chemical vapor deposition method. The fabricated film displayed absorption peaks at 325 nm excitation covering the entire visible spectrum range.[115] In another study, perovskite solar cells based on transition metal Ti, Ni, and Cd-doped BiFeO3, as a light absorber with graphene electrode have been investigated. The Voc of pure BiFeO3, Ti, Ni, Cd-doped BiFeO3 have been reported to be 0.49, 0.77, 0.56, and 0.49 V, respectively. A study of formation of thin films of pure and doped perovskites through three different processes—spinning, dipping, and spray process—has been carried out that revealed that Ti-based BiFeO3 in spinning process have given the best results.[312] Lead-free Ti-based perovskites have been investigated for their photovoltaic behavior.[311] Transition metal palladium-based lead-free perovskite Cs5PdBr6 nanocrystals have been reported with an average particle diameter of 2.8 nm and a thickness of 1–2 units cells exhibiting a narrow bandgap of 1.69 eV and outstanding stability toward light humidity and heat. The fast anion exchange method has been employed to synthesize Cs5PdI6 nanocrystals.[314]

Lead-free (1−x)(K0.44Na0.52Li0.04)(Ni0.05Ti0.05Sb0.04)O3−xSmAlO3 [x = 0, 0.001, 0.004, 0.008, 0.008] ceramics have been synthesized by a solid-state sintering method. The effect of doping of SmAlO3 on the phase structure and electrical properties of all the perovskite composition for reported values of x have been investigated thoroughly. From the study of XRD analysis, all the investigated composition reported a perovskite structure at the suitable sintering temperature. The enhanced electrical properties were obtained at the sintering temperature of 1150 °C.[315] Lead-free multiferroic (1−x)KNbO3−xCoFe2O4 composites have been synthesized by employing solid-state reaction method with x (0, 0.25, 0.5, 0.75, 1.0) mol. The careful study of XRD reveals that KNbO3 perovskite belong to an orthorhombic system, spinal CoFe2O4 belong to cubic system, and other compositions of x belong to mixed phase of KNbO3 and CoFe2O4. The high-resolution SEM analysis has shown that the morphology of KNbO3 and CoFe2O4 was modified by CoFe2O4 content. The composite 0.5KNbO3 0.5CoFe2O4 displayed a high value of coercivity and 0.5KNbO3 0.5CoFe2O4 and 0.75KNbO3 0.75CoFe2O4 displayed an enhanced value of dielectric constant.[316] At present, a lot of research is going on lead-free double perovskite materials to explore their potential as a light absorber in perovskite solar device. Double perovskite A2B′X4[A-Cs, MA, B′-Bi, Sb, B′-Cu, Ag, X-Cl, Br, I] have been investigated for their structural, optical, and stability properties.[317] The vapor-assisted method has been employed to synthesize double perovskite Cs2AgBiBr6 thin films with better morphology. The better quality of Cs2AgBiBr6 films has a photoluminescence lifetime of 117 ns. The fabricated n-p perovskite solar cell has reported a SPCE of 1.37% with a better stability of 90% after 240 h of storage under ambient conditions.[318] The diffusion of X halide anion in lead-free double perovskite Cs2AgBiX6 [X-Cl, Br, I], Cs2AgSbCl6, Cs2AgInCl6 has been investigated by using first principle calculations. The calculated values of formation energy of X-site vacancies are related to electronic configuration of B-site cations. The double perovskite Cs2AgInCl6 is having lowest vacancy formation energy due to unfilled s-orbital of In3+. The hysteresis loss in Cs2AgBiBr6 solar cells is attributed to the lowest energy barrier for X-site migration.[319] Double perovskite lead-free layered Cs2CuSb2Cl12 have been reported with a bandgap of 1 eV prepared by grinding of precursor salts at ambient conditions. A long range magnetic ordering is displayed by the synthesized perovskite at room temperature that plays a pivotal role in controlling the electronic properties of double perovskite Cs2CuSb2Cl16.[320] By using first principle calculations, lead-free double perovskite Cs5NaBiX6 [B-Sb, Bi, X-Cl, Br, I] have been synthesized and characterized for their electronic and optical properties. The simple solution method has been employed to prepare a layered MA3BiI9 perovskite and a composite layer of bismuth tri iodide (BiI3). By employing SEM and XRD techniques, the morphology of the active layer has been investigated that has a direct influence on performance of the perovskite device.[321] The high-temperature solid-state reaction method has been employed to prepare polycrystalline material of double perovskite Dy3NimO4 with a monoclinic structure. The high-temperature condition of the material is attributed to the presence of oxygen vacancies making it viable to use at different temperatures.[322]

9. Conclusion

The research in tin-based perovskites MASnX3 has revealed a direct bandgap of 1.20–1.35 eV, electron mobility of 2320 cm2 V−1 s−1, hole carrier mobility of 322 cm2 V−1 s−1, and long charge carrier diffusion length of more than 500 nm. The alteration of Br−/I− ratio in MASnI3−xSnBrx has resulted in large value of Voc (0.88 V) in MASnBr3 and JSC (12.33 mA cm−2) in MASnBr2. The absorption band can be tuned by altering the composition of halide anions in MASnX perovskites. However, Sn-based perovskites suffer from degradation in air due to oxidation of Sn2+ into Sn4+. The incorporation of additives has resulted in reduced oxidation and better stability in air. The A-site cation has a significant effect on photovoltaic performance. The use of diethylammonium (en) and FA+ at the A-site of ASnX3 has resulted in wider bandgaps and improved stability. An efficiency of 8% has been achieved for (FA)0.75(MA)0.25SnI3 with a Voc (0.61 V) and bandgap (1.33 eV). Germanium-based perovskites do have an optical bandgap of 1.63 eV, excellent hole and electron conducting behavior, and better stability in air. Using DFT calculations, it has been reported that with increase of size of halide anion, the bandgaps have decreasing values of 3.7, 2.81, and 1.61 eV, respectively. The replacement of the iodide content in AGeI3 by bromide results in enhanced photovoltaic performance and stability to a slight extent. Mixed Ge-based perovskite RbSn0.5Ge0.5I3 exhibits a better optical absorption and effective masses for higher carrier mobility and good stability in water. By engineering the size of A-site cation, its doping with another suitable cation and size of halide anion, it is possible to fabricate a Ge-based perovskite as an efficient light absorber. Although, bismuth-based perovskite (MA)3BiI6 has displayed low values of solar power conversion efficiencies up to 1.64 eV up to now, yet they have exhibited excellent stability in ambient air at room temperature and against exposure to humidity. The morphology of (MA)3BiI6 films can
be enhanced by addition of various concentration of NMP into the precursor solution that not only controlled the rate of crystallization but also enhanced the efficiency and stability in a relative humidity of 50–60%. The concentration of perovskite solution and substrate temperature also impacts its efficiency and stability. The wide bandgaps of lead-free perovskites can be engineered to a narrow bandgap by incorporating triiodide into P(4-methyl piperidinium)2Bi2I9(MP-Bi2I9) that exhibited a bandgap of 1.58 eV in comparison to 1.5 eV of MAPbI3. The various deposition methods have a direct influence on morphology of films. Cs4BiSb2Cl12 has displayed an efficiency of 8% with a pure crystalline phase and stability. Bismuth-based double perovskite like Cs4AgBiBr6 exhibited an indirect bandgap of 2.19 eV. The DFT calculations have further revealed that the family of 3D double perovskites have optical bandgap in the visible range and low carrier effective masses. Bismuth-based perovskites can be thoroughly investigated for enhancement in their efficiency as these materials have excellent stability in ambient air and in relative humidity. In antimony-based perovskites, the size of cationic or anionic species and the employed processing technique determine the structure. When A-site cation Cs+ is replaced by a smaller cation Rb+, a 2D layered phase is achieved with a formation energy difference of 0.25 eV in comparison to Cs-based counterparts. The addition of additive in 0D (MA)2SbI4 films has resulted in enhanced light absorption in the visible wavelength regions up to 400 nm. The use of chalcogenide and mixed perovskite materials can be an effective strategy for formation of efficient, cheap, and stable solar cells. Cs4CuSb2Cl12, besides having photo and thermal stability and resistance to humidity, have exhibited excellent photovoltaic properties. There has been a significant effect on photovoltaic parameters on substitution of Nb with Bi in 2D mixed layered perovskites (NH4)4(Sb1−xBix)4I12. By proper substitution of Bi into antimony-based perovskites, it is possible to fabricate light harvesters with high efficiency and stability. Copper-based perovskites usually form 2D layered structure owing to their smaller ionic radii. By proper tuning of Cl-/Br− ratio, the optical absorption of Cu-based perovskites can be extended in the near-infrared region. The (MA)2CuCl2Br2 and (MA)2CuCl0.5Br3.5 has reported a bandgap of 1.07 eV. The various deposition metals Ti, Ni, and Cd-doped BiFeO3 as a light absorber have been investigated for perovskite solar cells. The perovskite solar cells based on transition metals Ti, Ni, and Cd-doped BiFeO3 as a light absorber have displayed VOC values of 0.77, 0.56, and 0.49 V, respectively. By suitable selection of A and B-site cations and halide anions, their alteration in composition and synthesis method, it is possible to fabricate lead-free perovskites with maximum efficiency and stability without any toxic influence on environment.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

lead-free perovskites, photovoltaic parameters, stability

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