Review

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Issues, Challenges, and Future Perspectives of Perovskites for Energy Conversion Applications

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Abstract: Perovskite solar cells are an evolving technology owing to self-assembling and highly tunable bandgap properties of materials. In this context, thin films of perovskites have attracted immense attention and witnessed great advancement because of their low manufacturing cost. The key development in these devices is the conversion efficiency, which rose from 3.8% to 28%. The formulation of innovative materials with the proper replacement of lead in perovskites is imperative to mitigate lead toxicity. Here, we analyzed the challenges like material and structural stability, device stability under high temperature and humidity conditions, lifetime, manufacturing cost, etc. faced in the commercialization of perovskite devices. This review shows that challenges such as device engineering, performance stability against the harsh environment, cost-effectiveness, and environmental concern should be taken into consideration for the widespread acceptance of perovskite-based solar devices. In conclusion, we suggested that an enormous scope exists for exploring high-performance and long-lasting perovskites for energy applications.

Keywords: Perovskite materials; Solar cells; Energy conversion efficiency; Issue and challenges in commercialization

1. Introduction

Energy usage is considered one of the key indicators of the social progress index of development. Fossil fuels, namely oil, natural gas, and coal, are the most abundant and widely used energy sources for the generation of electricity. The continuing use of fossil fuels is having a serious impact on climate change, animal habitat destruction, and global warming [1]. Considering the environmental threats, many countries have committed themselves to the mitigation of greenhouse gas (GHG) emissions as a part of the 2015 Paris Agreement and are now focusing on replacing fossil fuels with renewable energy resources [1]. In recent years, there have been discussions on the energy transition toward sustainable renewable sources, which were taken forward at the COP26 conference in Glasgow, UK, in 2021 [2]. Solar and wind energy sources are considered clean energy sources for the future and are abundantly available worldwide. Undoubtedly, solar energy and solar-based devices are the most feasible alternatives to fossil fuels.

Various materials are utilized for the fabrication of solar cells that convert the solar spectrum into electrical energy. However, it is difficult for any photovoltaic (PV) cell to convert the entire spectral range into electrical energy. The most practically demonstrated and successfully commercialized material is the crystalline (c-Si) solar cell. Although this solar cell has been widely employed, it has several drawbacks, such as a low efficiency of 17% because of the Schokley Queisser limit, even though the theoretically estimated efficiency is 29% [3]. In this context, organometallic perovskites are viewed as the most promising alternative. Perovskite solar cells are accepted as the third-generation technology, which also incorporates dye sensitized (DSSC) and quantum dots (QD) solar cells. These perovskite materials are sensitive to visible solar radiation for the PV cell [4] and have an efficiency equivalent to the C-Si solar cell. In recent years, hybrid perovskites have exhibited high performance [5-7], and conversion efficiency of approximately 20% was achieved in PV cells [8-9]. Interestingly, the recent *data suggest* an incredibly rapid external quantum efficiency (EQE) improvement trend, particularly for tandem perovskite/CIGS (~25%) and perovskite/c-Si solar cells (~28%) [10-11].

This review article aims to discuss the perovskite materials with regards to energy conversion efficiency and stability. The evolution of perovskite materials is presented in Section 2. Section 3 describes the evolution of perovskite for solar cells, including inorganic and hybrid solar cells, whereas perovskite materials concerned with solar cell applications are discussed in Section 4. Issues and challenges, such as structure stability, device fabrication, lifetime, manufacturing cost, and practical alternatives to lead metal in perovskite, have been addressed in Section 5. Conclusions have been summarized in Section 6. We suggest that industrialization challenges such as device engineering, performance stability against harsh environments, cost-effectiveness, and environmental concern should be taken into consideration for the widespread acceptance of solar cell devices.

2. Perovskite Materials

The first inorganic perovskite material, calcium titanate ($CaTiO_3$) (the naturally occurring mineral), discovered by the Russian Mineralogist Perovskite in 1839, is the origin of perovskite and perovskite-based materials [12]. Pioneering studies on the structure of perovskites were performed by Victor Goldschmidt (1926) [13]. Subsequently, several synthetic perovskites were prepared and studied [14-15]. Approximately more than 40 naturally-occurring minerals in the form of oxides, halides, hydroxides, arsenide, and intermetallic compounds have been identified in the perovskite supergroup [16]. The classification of the perovskite system is presented in Figure 1.

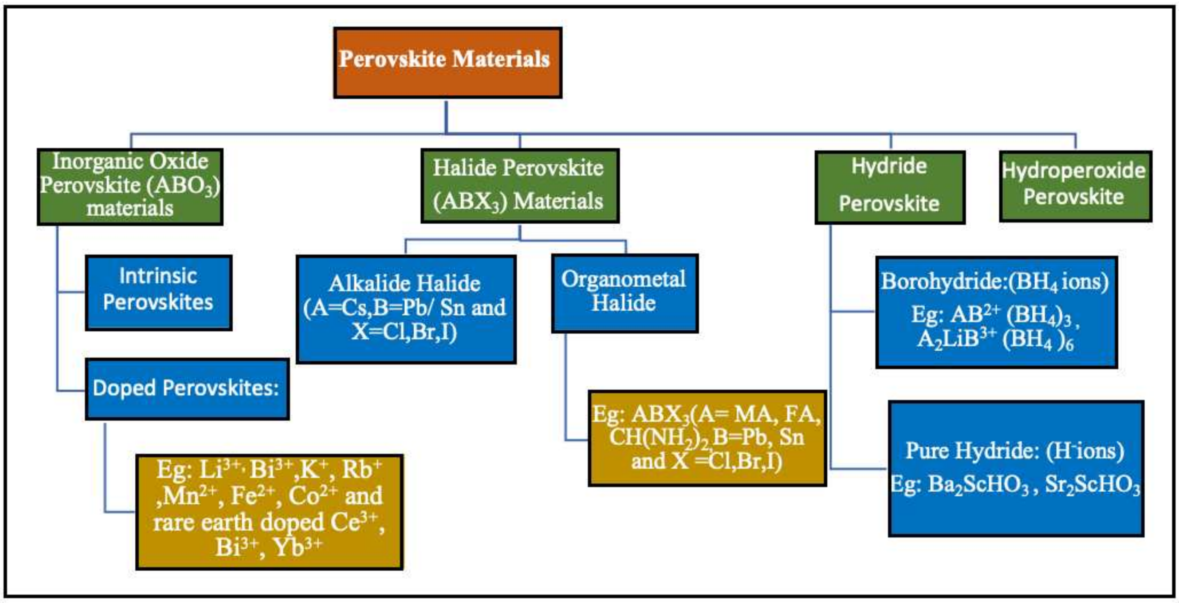

Figure 1. Classification of the Perovskite System.

Perovskites are very versatile materials and have been emerging as the rising star in the field of optoelectronics during the past decade, as displayed in Figure 2 [17]. Optoelectronic devices based on perovskites include solar cells, photodetectors, lasers, electrochemical cells, and light emitting diodes. Revolutionary applications of these devices are in the fields of energy harvesting and conversion, imaging and sensing, X-ray detectors, display and communication, and manufacturing and medicine [17, 18].

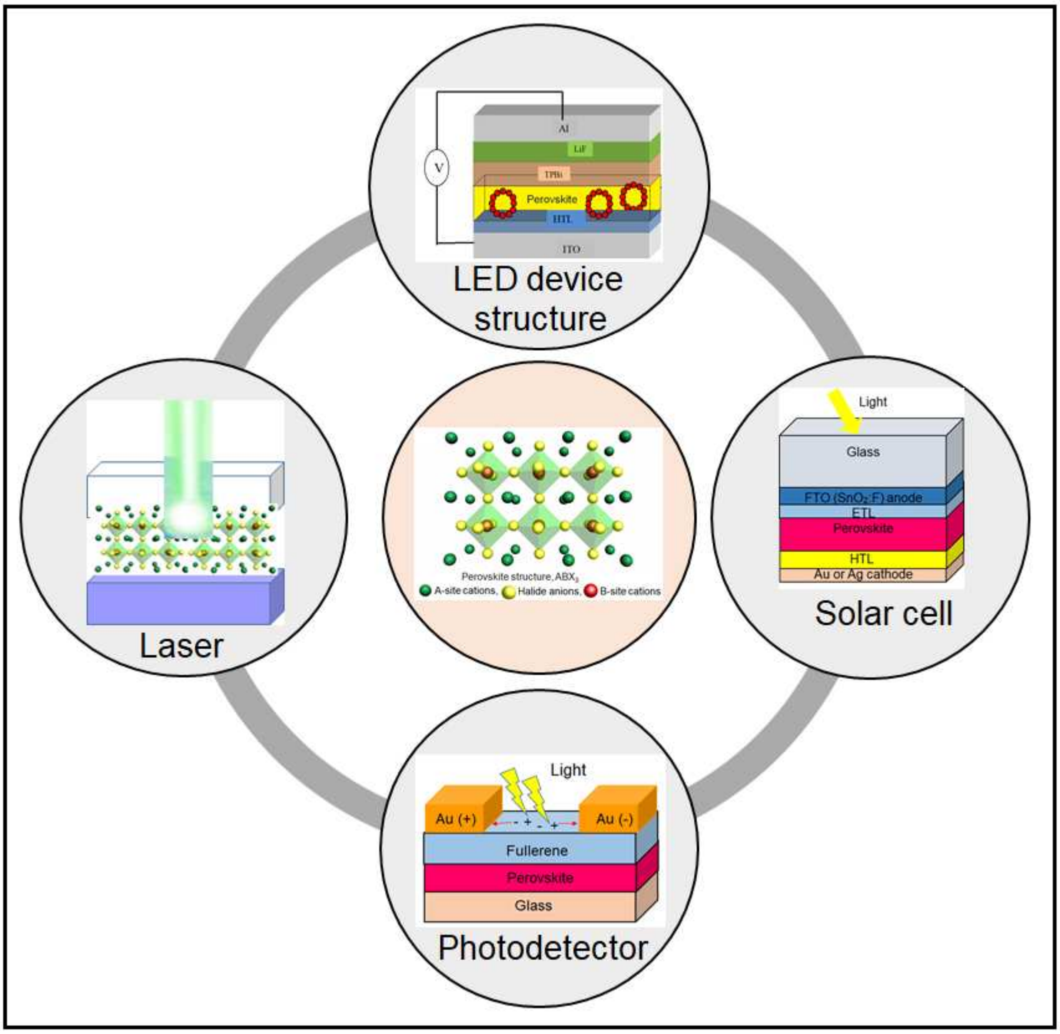

Figure 2. Optoelectronics devices based on metal halide perovskite materials and revolutionary applications.

Perovskite materials have several distinct properties. The key electrical, physical, and optical characteristics include long-range ambipolar behavior of charge transport, small exciton-binding energy, a high-value dielectric constant, a high-absorption coefficient, ferroelectric properties, a tunable bandgap, and ease of manufacturing at low temperatures. Such favorable attributes of these materials have attracted immense interest for optoelectronic and PV applications [19]. Mixed lead halide-layered perovskite materials have been explored for usage in thin-film light-emitting diodes (LEDs) and also for field-effect transistors (FETs) because of the strong excitonic properties of these materials.

Halide perovskites (HPs) are recognized as the most favorable and accepted materials in PV, thermoelectric, optoelectronic radiation detection, and emission optoelectronic applications owing to their exceptional optical and excitonic properties [20-22]. Among organic halide perovskite materials, methylammonium lead triiodide ($MAPbI_3$) is commonly used in PV applications. Its stable structure and simple and inexpensive manufacturing process make lead halide perovskites the preferred material for the mass production of solar panels. Metal halide perovskites have revolutionized the field of solution-processable devices and opened the way for the development of efficient flexible PV cells [23]. Ge et al. reviewed the recent progress in multidimensional metal halide perovskites for PV applications and highlighted the challenges in the field [24].

The hybrid metal halide perovskite materials exhibit promising optoelectronic properties. Zhu and Gong (2021), in this article, opined that 3D halide perovskites possess unique potentials for

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efficient optoelectronic applications [25]. The researchers also summarized the preparation process of low-dimensional halides and addressed the systematic scientific methodology and technical challenges in the 3D perovskite materials, like inferior long-term stability, which slow down practical applications.

3. Evolution of Perovskite for Solar Cells

Figure 3 (a) shows the block diagram of perovskite solar cells. The operation principle of multilayer solar cells is illustrated in Figure 3 (b). The basic device structure contains a radiation-absorbing perovskite layer squeezed in between the anode, usually F-doped SnO_2, and a high-work-function cathode, like Ag or Au metal. The light absorption by the solar cells is due to the formation of excitons (a quasiparticle comprising a pair of positive (hole) and negative (electron) charges) in their absorbing layer (the perovskite material layer). The electrons get excited by the incident photons to a higher energy level and leave the holes behind. Often, the charge transport layers are used in devices to facilitate the movement of the accumulated charges that generate an electric current in the circuit.

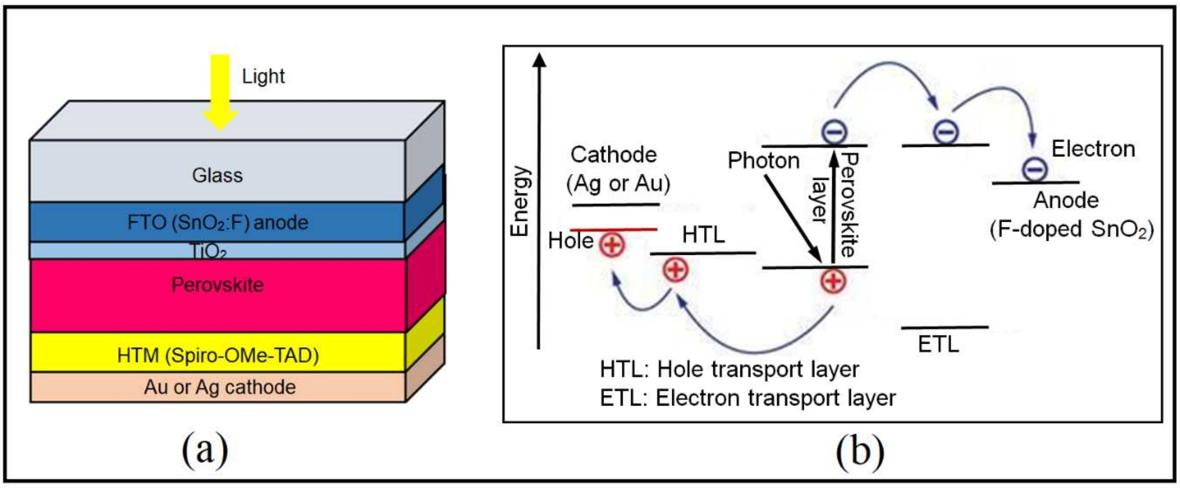

Figure 3. (a) Schematic diagram of perovskite solar cells. (b) Operational Principle of the Multilayer Solar Cell.

During early usage, the perovskites were created on DSSC and combined with a thin perovskites layer on a substrate of mesoporous TiO_2 that acted as an electron collector, which had a power conversion efficiency (PCE) of 3.8% [26]. Later, using the same concept of DSSC, Park et al. (2011) obtained a PCE of up to 6.5% [27]. An efficiency value of 9.7% was subsequently achieved using a solid-state electrolyte that operated like a hole transport material (HTM) [28]. Heo et al. (2013) reported PCE up to 12% with the use of an HTM-based perovskite solar cell (PSC) and poly(triarylamine) layers [29]. The obtained efficiency was improved further to 12.3% with the use of a mixed halide $CH_3NH_3PbI_{3}$-xBrx perovskite structure [30]. The efficiency of the mixed halide was attributed to the introduction of small-radius bromide (Br) ions and the phase transition from tetragonal to cubic structure, which provided stability to perovskite.

Later, improvement in efficiency (up to 15.2%) with the introduction of the pinhole-free perovskite film using a non-halide ($PbAC_2$) under the direct illumination of sunlight was achieved by Zang et al. (2015) [31]. Such a substantial efficiency improvement (>15%) and stability were reported by several researchers when the devices were fabricated with PbX_2 (X=Cl and I) using solution deposition and thermal evaporation techniques [32-35]. This PCE performance was enhanced up to 16.2% by varying the energy bands of the mixed halides [36] and modifying the thickness of the perovskite-infiltrated TiO_2 frame link to the constant perovskite layer [37]. Shin et al. (2017) have shown that the adjustment of the band arrangement of HTM/ETM (hole/electron transport material) improves the efficiency from 19.3% to 20.1% [38]. The contribution of various institutions and scientific laboratories to the development of PSCs is displayed in Figure 4.

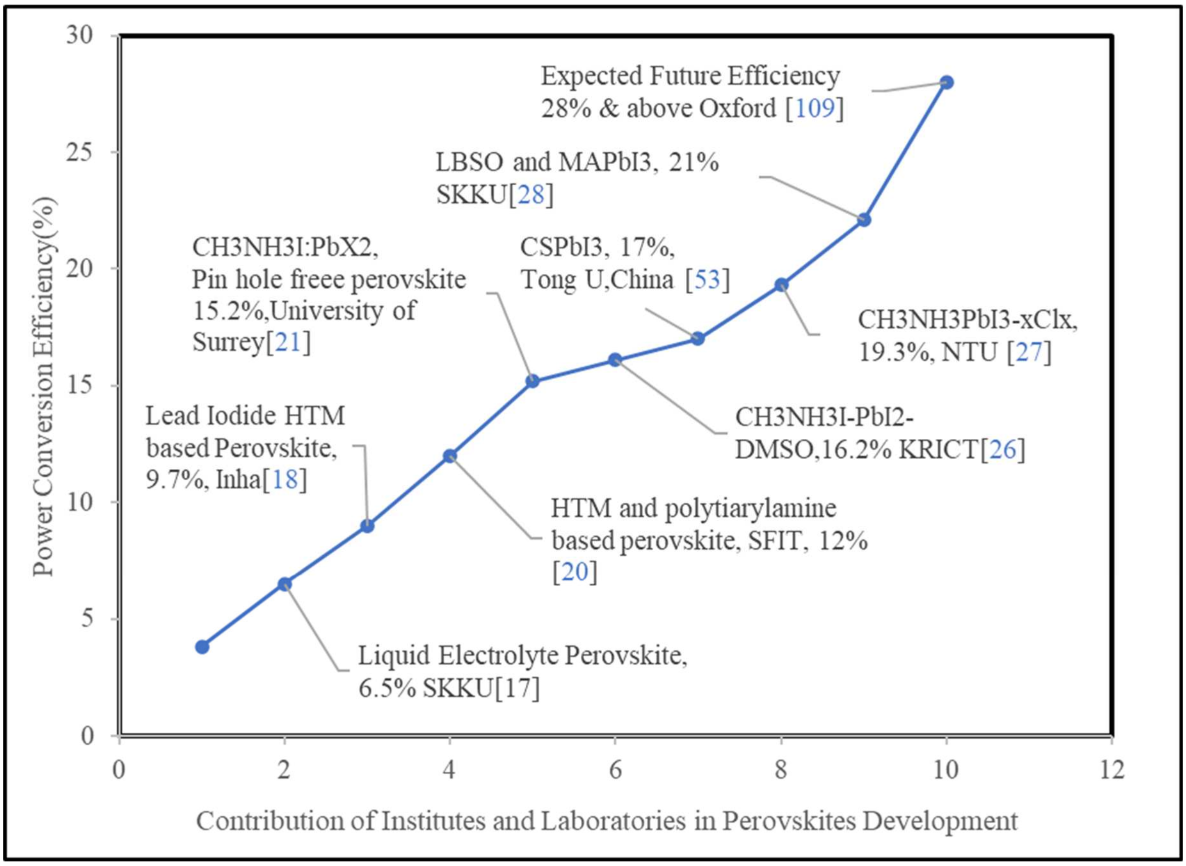

Figure 4. Contributions of Institute and Laboratories toward the Evolution of Solar Cells using Perovskite Materials.

A dramatic rise in the efficiency from 3.8% (2009) to 20% (2017) of perovskite solar cells was achieved with solid-state thin-film design, modified film formation technique, optimization of film thickness and morphology, interface engineering, and the use of the mixed-halide perovskites as a photon-absorbing layer in the cell structures [39].

3.1. Inorganic Perovskites Solar Cells

Inorganic perovskite is commonly referred to as the ABX_3 compound, wherein A refers to the cations (Cesium: Cs^+ ions) occupying the cubo-octahedral site and BX_3 occupies the octahedral site. In this structure, B is the anion (Pb^{2+} ions) and X= Cl, Br, or I. Table 1 lists the developments in $CsPbX_3$(Br, I, Cl) perovskite materials, fabrication processes employed, solar cell device structure, and conversion efficiency achieved [40 – 45].

Table 1. Developments in Inorganic ABX_3 Compounds in Terms of Efficiency.

S. No.	Inorganic Perovskite	Method	Solar Cell Device Structure	Efficiency (%)	Ref.
1	$CsPbI_3$ and its derivative perovskite	Solvent controlled growth	Stable α-phase $CsPbI_3$. Device structure: (ITO)/SnO_2/$CsPbI_3$/Spiro-OMeTAD/Au	15.77	[41]

	solar cells (PSC)				
2	$CsPbI_3$	PCE-based PSC via surface termination of the perovskite film using phenyl trimethyl ammonium bromide (PTMBr)	Highly stable phase due to the use of PTMBr treated with $CsPbI_3$. Device layers: FTO/c: TiO_2/perovskite/Spiro-OMeTAD/Ag	17.06	[42]
3	$CsPbI_3$	Formamidium (FA) iodide (FAI)-coated quantum dots	Tio_2/FAI-coated $CsPbI_3$/Spiro-OMeTAD/ MoO_x/Al	10.7	[40]
4.	$CsPbI_2Br$	Fabrication of ZnO/C60 bilayer electron transport layer in inverted PSC PCE	FTO/NIO_x/ $CsPbI_2Br$/ZnO @C_{60}	13.3	[43]
5	$CsPbI_2Br$	Introduction of $InCl_3$ to enhance the efficiency of inverted PSC	Yellow stable (δ-phase). Device structure: FTO/NiO_x/perovskite/ZnO@C_{60}/Ag using $InCl_3$:$CsPbI_2Br$ perovskite	13.74	[44]
6.	$CsPbI_xBr_{3-x}$	Lewis base, 6TIC-4F certified, and the most efficient inverted inorganic PSC with improved photostability reported till date.	Inverted layer with structure FTO/NIO_x/ $CsPbI_xBr_{3-x}$ /ZnO/ C60/Ag	16.1 certified 15.6	[45]

3.2. Hybrid Perovskite Materials Solar Cell

Hybrid perovskites are an emerging field of semiconductor materials. Favorable attributes are affordable, solution-based semiconducting materials with promising optoelectronic properties. Tunable bandgap [46-47], strong absorption coefficient, small excitation binding energy [48-49], and balanced mobility of the charge carriers with minimal defect formation characteristics make them suitable for application in solar cells and LEDs [45, 50]. The rapid advancements in perovskite materials have enhanced the efficacy of solar cells from 3.8% to 22% in a very short span [27, 29, 37]. The intensive developments in methylammonium (MA) lead halide perovskites with respect to efficiency and the trials of various HTMs have led to considerable progress in thin-film optoelectronics. The development of hybrid PSCs with PCE using various HTMs has been described in Table 2 [27, 36, 37, 51-54].

Table 2. Progress in Hybrid Perovskite Solar Cells and Power Conversion Efficiency:.

SN	Hybrid Perovskite	HTM	Device Structure	Efficiency (%)	Ref.
1.	$CH_3NH_3PbI_3$	I^-/I^{-3}	$CH_3NH_3PbI_3$ Quantum dots (QD)/TiO_2 substrate	6.5	[27]
2.	$CH_3NH_3PbI_3$	CuI	TiO_2/ $CH_3NH_3PbI_3$/ spiroOMeTAD	6.0	[51]
3.	$CH_3NH_3PbI_{3-x}Cl_x$	NiO	FTO/NiO/CuSCN/ $CH_3NH_3PbI_{3-x}Cl_x$/ PCBM/Ag	7.3	[52]
4.	$CH_3NH_3PbI_3$	CuSCN	TiO_2/ $CH_3NH_3PbI_3$/ CuSCN/Au	12.4	[53]
5.	$CH_3NH_3PbI_{3-x}Br_x$	PTAA	TiO_2/ $CH_3NH_3PbI_{3-x}Br_x$/DMSO/PTAA/Au	16.2	[36]
6.	$CH_3NH_3PbI_3$	NiO_x	ITO/NiO_x/ $CH_3NH_3PbI_3$/PCBM/Ag	16.47	[54]
7.	$CH_3NH_3PbI_{3-x}Cl_x$	spiroOMeTAD	ITO/PEIE/TiO_2 $CH_3NH_3PbI_{3-x}Cl_x$/ spiroOMeTAD/Au	19.32	[37]

3.3. Materials Requirements for High Performance Solar Cell Devices

Fabrication of perovskite film with good quality, robustness against harsh environmental conditions, and structural stability is imperative for the high-performance device of solar cells. Many properties of perovskites, such as direct bandgap, phase purity and stability at room temperature, illumination, and degradation at high temperatures, have been well studied. Hence, some other vital properties of perovskite materials, which enable better performance compared with other semiconductors and dyes, have been highlighted here. These properties include the maximum absorption range, the optimal bandgap required for the excitation coefficient, the dispersion of charge carriers to enhance the intensity, photoluminescence, and electroluminescence emission spectra. Perovskites enjoy a wide absorption range, including the visible and near-IR (NIR) regions. In this context, organometal halides are advantageous over dyes. $CH_3NH_3PbI_3$ perovskite absorbs the entire range of the visible spectrum with a halide film about 600 nm thick [55]. $CH_3NH_3PbI_3$ shows better absorption, which is the main requirement for any solar material. Moreover, this material has a bandgap of 1.55 eV, which is almost equal to the bandgap of 1.4 eV. This property, combined with an extinction coefficient value of 1.5×10^5 $(mol/L)^{-1}.cm^{-1}$ at around 550 nm, makes $CH_3NH_3PbI_3$ an excellent solar radiation-absorbing material [55] and gives an exceptional quantum efficiency at 800nm in the solar cell. Several researchers have discussed the ambipolar behavior of $CH_3NH_3PbI_3$ perovskite. A mesoporous $TiO_2/CH_3NH_3PbI_3$ solar cell with 5.5% efficiency [56] displays a p-type nature. $MAPbBr_3$-based LEDs have been demonstrated to reduce metallic grain impurities. The nanograin of $MAPbBr_3$ is approximately 100nm thick with an EQE of 8% [57]. The mesoporous $ZnO_2/CH_3NH_3PbI_3$ solar cell exhibits n-type behavior with 10.8% efficiency [34]. Other researchers have shown that $Al_2O_3/CH_3NH_3PbI_{-x}Cl_x$ possesses an n-type charge transport characteristic [30, 37, 52, 57]. The organometal halide perovskite has a high mobility of charge carriers and generates charges quickly, which simplifies the manufacturing process [58]. The charge transport characteristics are mainly responsible for the long-range light absorption in relation to the charge carrier's diffusion length. Methylammonium lead iodide ($MAPbX_3$) perovskite possesses significant optical and electronic properties [59, 60]. The absorption starts at 800nm and fairly covers the visible spectrum region, with separated free cations even at room temperature [61, 62]. Iodine can be a good substitute for chloride (Cl^-) and bromide (Br^-) because of the continuous tuning of the bandgap, which covers most of the visible spectrum [63 - 66]. The large bandgap value of 2.2 eV and binding energy of 150 meV of bromide in $CH_3NH_3Br_3$ in comparison with $CH_3NH_3I_3$, which has a bandgap of 1.5 eV and binding energy of 50 meV, limit the light absorption up to 550nm and hence lower the photocurrent [65] and also restrict the PCE [67]. The classification of perovskite materials based on their characteristics is presented in Table 3.

Table 3. Classification of Perovskite Materials based on their Characteristics.

Perovskite	Characteristics	Behavior Response
$CsPbI_3$	Bandgap	Spin-orbit coupling approximation 1.16eV can be reduced to 0.39eV
	Binding energy	169eV
	Photoluminescence	$\lambda_{em} = 680nm$, $\lambda_{ex} = 365nm$
$CH_3NH_3PbBr_3$	Absorption	800–550nm
	Bandgap	2.2eV
	Binding energy	150meV
	Photoluminescence	Emission at shorter wavelength owing to larger bandgap $\lambda_{em} = 560nm$
$CH_3NH_3PbI_3$	Absorption	800nm to complete visible spectrum
	The thickness of the film	600nm
	Bandgap	1.55eV comparable with the optimal band gap 1.4eV
	Binding energy	50meV
	Photoluminescence	Emission at longer wavelength owing to small bandgap ($\lambda_{em} = 770nm$ for $\lambda_{ex} = 546$ nm)
Ambipolar behavior	Mesoporous TiO_2/ $CH_3NH_3PbI_3$	*p*-type charge transport. Solar efficiency of 5.5%
	Mesoporous ZnO_2/ $CH_3NH_3PbI_3$	*n*-type charge transport. Solar efficiency of 10.8%
	Dispersion range	130nm and 100nm. 1100nm and 1200nm in $CH_3NH_3PbI_{3-x}Cl_x$

The advancements in solar perovskites and increase in their conversion efficiency from 3.8% to 26% witnessed over the past decade could be attributed to the frantic research and mass production of perovskite materials. Highly stabilized solar cells with low voltage loss have also been investigated recently [68]. A device with long-term stability has displayed a PCE of approximately 25.2%. This value is near the C-Si efficiency of 26.2%, which has dominated the market as per several reports. The Oxford PV made use of tandem solar perovskites, achieving lab efficiency of up to 28% [69], wherein all perovskites in tandem exhibited comparable tandem efficiencies.

4. Perovskite Materials Concern for Solar Cell Applications

Lead-free perovskite seems to be the most appropriate alternative. Intensive research and technological advancements in lead-based perovskites are at their pinnacle and progressing toward commercialization. The modified compounds are required to have optoelectronic properties that should be at par with Pb-based perovskites and fulfill the criteria for mass production and commercialization. Tin (Sn), Bismuth (Bi), Antimony (Sb), Germanium (Ge), Double halide perovskite materials, and chalcogenide perovskites could become favorable compounds in perovskite solar cell applications.

Sn-Based Solar Cells

Several researchers have attempted to develop Sn-based perovskites, such as Cs_2SnA_6, (A = Cl, Br, or I) [70 – 72] that are stable in the presence of moisture in the 4+ oxidation state. Some selected Sn-based PSCs and their properties are listed in Table 4 [73 – 75].

Table 4. Summary of Selected Sn-based Perovskite Materials and their Characteristics.

Perovskite Materials	E_g (eV)	Voc (V)	Jsc (mA-cm^2)	FF	PCE (%)	Ref.
$MASnI_3$	1.3	0.68	16.3	0.48	5.23	[73]
$MASnI_{3-x}Br_x$	1.75	0.82	12.3	0.57	5.73	[73]
$MASnIBr_{0.8}Cl_{0.2}$	1.25	0.38	14	0.57	3	[74]
$CsSnI_{2.9}Br_{0.1}$		0.22	24.16	0.33	1.76	[75]

(where, E_g - Energy Band fap, V_{OC} – Open Circuit Voltage, J_{sc} – Short Circuit Current Density and FF- Fill Factor).

Bi-Based Solar Cells

Bi^{2+} is a potential candidate for optoelectronic applications. A report on $MA_3Bi_2A_9$ (A = Cl, Br, or I) quantum dots, produced by synthesizing using a ligand-assisted recrystallization approach, established that the tunable band can be varied from 360 to 540 nm. This wide range of variation is due to the anion composition, which gives intense emission at 423 nm with a PL quantum yield (PLQY) of around 12%. At present, a few successful results have been obtained with the Bi perovskite materials, which hold promise for replacing the Pb-based perovskites. However, some research observations have implied unfavorable results, such as a broad bandgap, low performance, and more internal defects in Bi-based perovskite materials. Some Bi-based PSCs and their properties have been shown in Table 5 [76 – 79].

Table 5. Summary of Selected Bismuth Perovskite Materials and their Characteristics.

Perovskite Materials	E_g (eV)	V_{oc} (V)	J_{sc} (A-cm^2)	FF	PCE (%)	Ref.
$Cs_3Bi_2I_9$	2.2	0.53	0.58	0.5	1.09	[76]
$MA_3Bi_2I_9$	2.1	0.83	3.0	0.79	3.17	[77]
$MA_3Bi_2I_9$	0.83	0.83	3.0	0.79	1.64	[78]
$FA_3Bi_2I_9$	2.19	0.48	0.11	0.46	0.022	[79]
$MA_3Bi_2I_{9-x}Cl_x$	2.4	0.04	0.18	0.38	0.003	[77]

(where, E_g - Energy Band fap, V_{OC} – Open Circuit Voltage, J_{sc} – Short Circuit Current Density and FF- Fill Factor).

Sb-Based Solar Cells

Sb is a heavy metal of low toxicity that belongs to the same element group as Bi^{3+}. Sb^{3+} cations possess an identical electron lone pair as Pb^{2+} and are therefore likely to replace Pb in the perovskite materials. The bandgap of inorganic $Cs_3Sb_2I_9$ is 2.05 eV and shows absorption comparable to that of the hybrid Pb-based perovskite $CH_3NH_3PbI_3$. This material exhibits higher stability in air compared with $CH_3NH_3PbI_3$. The thin films of $(CH_3NH_3)_3SbI_9$ demonstrated a photosensitive bandgap of 2.14 eV and PL at 1.58 eV.

Ge-Based Solar Cells

Another class of materials are the Ge-based inorganic and hybrid perovskites. The experimentally measured bandgap values for $CsGeI_3$, $MAGeI_3$, and $FAGeI_3$ are 1.66 eV, 1.9 eV, and 2.2 eV [80], respectively. Thus, Ge materials possess desirable optoelectronic properties and could become a potential replacement for Pb in perovskite materials. Some selected Ge-based PSCs and their properties have been presented in Table 6 [81 – 83].

Table 6. Summary of Selected Ge-based Perovskite Materials and their Characteristics.

Perovskite Materials	E_g (eV)	V_{oc} (V)	J_{sc} (A-cm^2)	FF	PCE (%)	Ref.
$CsGeI_3$	1.63	0.074	5.7	0.27	1.1	[81]
$MAGeI_3$	2.2	0.15	4.0	0.3	2.0	[82]
$MAGeI_{2.7}Br_{0.3}$		0.46	3.11	0.48	5.7	[83]

(where, E_g - Energy Band fap, V_{OC} – Open Circuit Voltage, J_{sc} – Short Circuit Current Density and FF- Fill Factor)

Double Perovskite Solar Cells

Computational investigations on the hypothetical perovskite with the general formula $Cs_2BB^{3+}X_6$ (called double perovskite) showed promising results with a bandgap in the visible region and a low effective mass [84]. McClure et al. reported the synthesis routes for the lead-free hybrid perovskites $Cs_2BiAgCl_6$ and $Cs_2BiAgBr_6$ [85]. Whereas Wei Fengxia et al. showed the synthesis of $(CH_3NH_3)_2KBiCl_6$ double halide perovskite [86]. Lijun Zhang et al. (2017) [87] proposed the new formula $A_2B^+B^{3+}X_6^{VII}$ (A = Cs^+, B^+ =Na^+, K^+, Rb^+) from group IA or (Cu^+, Ag^+, Au^+) or (In^+, Ti^+) from group IIIB, B^{3+} = (Bi^{3+}, Sb^{3+}), and X = (F^-, Cl^-, Br^-, I^-). They identified 64 such combinations and optimized them to 11 compounds with robust stability, which can be considered promising candidates for lead-free PVs. Furthermore, two compounds identified using computational methods, namely $Cs_2InSbCl_6$ and $Cs_2InSbCl_6$, with bandgaps of 1.02 eV and 0.9 eV, respectively, showed theoretical solar efficiency comparable to that of $CH_3NH_3PbI_3$.

Chalcogenide Perovskites Solar Cells

Very recent computational simulations have proposed a new class of chalcogenide perovskites [88]. Limited studies have been presented on these perovskite materials, and some materials, such as $BaZrS_3$ [89], $SrZrS_3$ [88], $BaHfS_3$ [88], and $SrHfS_3$ [89], have been synthesized. These materials possess bandgaps and absorption coefficients that are appropriate for solar devices. Shallow point defects are observed in these materials, which open the chance of fine-tuning charge transport and photosensitive properties. The actual experimental work is likely to open a new era in fabrication and thin-film technology and provide tailored materials for solar applications.

In summary, the merits and demerits, including challenges, of these new generations of perovskite materials have been presented in Table 7. The PCE evolution with next-generation materials has been depicted in Figure 5.

Table 7. Summary of Merits, Demerits, and Challenges in Next-generation Materials.

Materials	Merits	Demerits and Challenges
Tin (Sn) based perovskites	The optical bandgap is in the near infrared region, has a comparable ionic radius (1.35 Å) to Pb^{2+} (1.49 Å), and exhibits stability against moisture. Sn-based materials possess stability	Sn^{2+} may be as hazardous as Pb^{2+} and, therefore, may also face the same challenges that Pb-based perovskites are facing today.

	for 3800 hours. Among all lead-free materials, this material has presently achieved the highest efficiency.	
Bismuth (Bi) based perovskites	Bi^{2+} has the same electronic configuration as Pb^{2+} (ns^{2}). Inorganic Bi^{2+}-based materials show promising stability, are insoluble in water, are not toxic to the environment, are cost-effective, and have the potential to overcome most of the challenges that are faced by Pb in terms of industrialization.	has a broad bandgap, low performance, and more internal defects. Organic compound stability is relatively low. The lowest power conversion efficiency (PCE) achieved so far in comparison with other materials Needs a more promising research direction.
	Increasing quantum yield and PCE can make this candidate an immediate replacement for Pb in the near future.	
Antimony (Sb) based perovskites	Sb^{3+} compounds show stability in the presence of air, and the bandgap is also comparable to that of Pb (2.14 eV). They are insoluble in water, and Sb^{2+} possesses good charge transport properties owing to the small bandgap.	$(CH_3NH_3)_3SbI_9$ may face the challenges of energetic disorder and low photocurrent density. low-hopping mechanism for charge transport owing to the large bandgap.
Germanium (Ge) based perovskites	These are leading materials in the semiconductor industry and possess good optoelectronic properties. Moreover, they are lightweight and less toxic to the environment. They are stable in an inert atmosphere.	Decomposes easily in the air. It is not a cost-effective material.
Double halide perovskites	Robust stability and a direct bandgap of 0.9–1.02 eV.	Most of the research is based on the computational method.

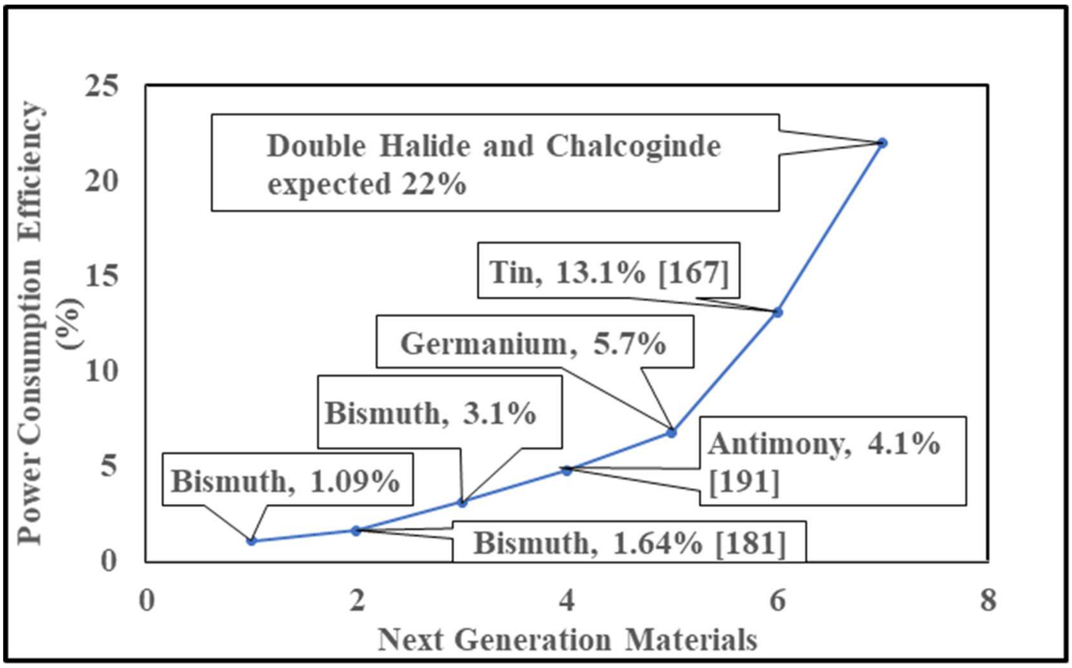

Figure 5. Development of Next-Generation Materials in terms of Power Conversion Efficiency.

5. Issues and Challenges in Perovskite Solar Cells

Substantial experimental and theoretical research has been made in learning and understanding the materials structure, device stability, efficiency, and complex composition. In recent years, perovskite materials and technology have taken a step toward manufacturing and have explored the market for the commercialization of perovskite solar cell devices. Wang et al. opined that the mass production of PSCs is not yet feasible due to various factors [90]. Challenges faced by perovskite solar cells are (i) high-quality perovskite layer fabrication with low cost and large-scale reproducibility, (ii) the choice and deposition of charge extraction layers, and (iii) the fabrication of bottom and top electrodes using low-cost processes. These issues need to be addressed to build small- and large-area PSC devices. In a review report, Yang et al. presented the advancement of efficient large-area PVs with stability for commercialization [91].

Furthermore, several concerns, such as lifetime, stability, lead toxicity, environmental contamination, and cost-benefit, are fundamental factors for the effective commercialization of perovskite solar cells. Perovskite compounds have a great tolerance to crystalline defects because of the ionic bonding, and thin films with high crystallinity can be fabricated at low temperatures only. Further, these materials have low decomposition temperatures, making them less thermally stable than Si [92]. Recently, Lin et al. summarized the issues, such as high stability and long lifetime, lead toxicity, fabrication repeatability, large-area fabrication, and flexible devices [93]. Metal halide perovskite solar panels merits and demerits are shown in Table 8.

Milić et al. (2021) observed that hybrid perovskites are affected by external factors such as air and moisture, photo-stability, and device operating voltage, thus resulting in various degradation routes [94]. Various strategies to overcome these instabilities, such as the use of low-dimensional hybrid perovskite materials, were proposed. Low-dimensional materials include layer-by-layer stacks of 2D perovskite and organic layers that are separated by hybrid perovskite slabs. Such a structure is more stable in ambient conditions and in ion relocation.

Although inorganic perovskites exhibit higher thermal stability, they have poorer phase stability than their hybrid counterparts. This is associated with the strain in the lattice and voids within the inorganic perovskite material crystals. In a recent review, Xiang et al. (2021) summarized and discussed the stability and lifetime mechanisms of inorganic perovskites with regard to heat, humidity, and oxygen [95]. Minimizing the vacancies and strain during the film processing may be a possible way to address the stability concerns related to both intrinsic and extrinsic factors. Challenges that need to be overcome strategically to transform perovskite modules into marketable PVs include stability, lead leakage, and outdoor testing of the modules, as discussed by Cheng et al. (2021) [96].

Table 8. Merits and Demerits of Halide Perovskite Solar Panels.

Merits	Demerits
Hybrid perovskites with the general formula ABX_3 (A = organic cation, B = divalent metal, and X = halogen or pseudo-halogen) are used.	*External factors*, such as water, heat, humidity, and sunlight, inherently degrade the stability of the *active layer* of perovskite solar panels.
Easy, low-cost manufacturing processes make perovskite the obvious choice for mass production.	*Water sensitivity* causes irreversible damage to perovskite materials.
The PCE of perovskite solar cells is high.	*Heat*: Lead halides show an inability to sustain thermal stress. Therefore, the perovskite structure degrades under heat and creates halogen gases that are the source of the formation of B metals (lead, tin, germanium, etc.) on the perovskite film.
Hybrid perovskite film solar panels are confirming candidates for power generation in the near future.	***Oxygen and light***: Prolonged exposure to air and light photons adversely degrades the longevity of the solar panel.
Conversion energy loss is less in perovskite solar cells compared with other cells.	*Scalability and efficiency* on large-area perovskite are comparatively small. The technology is yet to be effectively transferred from the *laboratory* to the *industry*.

It may be mentioned here that lead is likely to be widely used in perovskite PV industries in the future. When the PSC panels die, the lead metal could possibly leach into the ecosystem, causing contamination of the air, earth, and groundwater. The major challenges like material stability, device fabrication, lifetime of the devices, manufacturing cost, lead toxicity, best practices to overcome these challenges, and viable alternatives to Pb metal have been discussed below.

5.1. Perovskite Structural Stability Perspective

The thin film of perovskites is polycrystalline and can vary with unit cell orientation. The thin film structure of the perovskite materials is important for the stable operation of any device. A small alteration in the synthesis route and formulation can lead to a remarkable change in texture and morphology, which exert severe impacts on the device's performance. Therefore, the production of efficient and stable perovskite materials for the solar cells faces a serious challenge in defining the structure. Liu et al. (2020) examined the instability and phase behavior of $FAPbI_3$ and showed that it is highly efficient but shows instability in air and decays rapidly in a hexagonal structure [97]. Schmidt-Mende et al. (2021) [98] suggested *in situ* real-time scattering measurement during the film formation to obtain a better understanding of the intermediate phases formed during the process. *The hybrid perovskite is expected to be highly ordered and likely to be the better alternative for the reliable operation of devices.*

5.2. Device Fabrication Issues

The spin-coating technique is commonly used for the deposition of a perovskite layer on the substrate in solution-processed device production. During the preparation, the solvent interacts with the precursor and forms halide complexes. The solvent plays a vital role and influences various properties of the precursor, such as its i) solubility; ii) evaporation rate; iii) viscosity; iv) crystallization; and v) formation of the intermediate phase. The formation of several complexes occurs with the use of strong binding solvents, like dimethyl sulfoxide (DMSO). The *weakly interacting solvents* allow strong interaction among the starting ingredients. This leads to the creation of the intermediate phase and its subsequent conversion into the perovskite phase, which allows the rapid formation of the perovskite phase upon evaporation [99]. Whereas strong-interacting solvents usually require annealing at a higher temperature for a few minutes to obtain the pure perovskite phase [100]. The formation of these complexes can be avoided by adding a few polymer additives [101, 102]. To overcome these challenges in the solution process, many reports have highlighted the step-by-step mechanism of thin-film formation.

5.3. Lifetime and Stability under High Temperature and Humidity

Most investigations and results reported by researchers for perovskite technology are focused on color, purity, and efficiency. However, the perovskite material and hence the stability of devices in harsh environmental conditions, such as high temperatures, weather fluctuations, and high humidity, are crucial factors to be considered seriously for commercialization. Therefore, it is vital to address the concerns of stability issues in order to achieve high efficiency and high durability simultaneously. Prolonged exposure to high temperatures or illumination and to moisture in the air result in the degradation of the perovskites [103]. The device's performance is susceptible to oxygen, as the perovskite layers degrade when they meet oxygen [103, 104]. Many researchers have argued that moisture, atmospheric oxygen, heat, etc. are possible causes for the degradation of PSCs. Whereas Wang et al. (2017) stated that PSC's degradation is due to the material’s natural properties [105]. Iodide-based perovskites like $MAPbI_3$ generate a gaseous state of iodine (I_2) that results in the degradation of the perovskite material. Furthermore, the acid-based chemical process used in the deposition of $ZnO/MAPbI_3$ layers causes degradation. TiO_2 and SnO_2, used in solar cell manufacturing, demonstrate better stability, but their excessive use causes degradation when exposed to UV radiation and leads to defects [106]. The morphology of spiro-MeOTAD and additives restricts its stability. Also, the commonly used Au electrode atoms diffuse at high temperatures via spiro-MeOTAD, causing degradation [107]. The use of carbon electrodes is found to be highly practicable for the device's stability [108].

Compared with the hybrid organic-inorganic perovskites, all inorganic lead halide perovskites, such as $CsPbI_3$, exhibited better thermal stability and, hence, attracted the attention of several researchers. But their low structural stability (phase stability) under ambient conditions limits their practical applications [109]. To improve longevity, the formation of 2D and 3D perovskites was suggested as a possible alternative. Next, the long-term stability of PSCs under ambient conditions can be augmented by using proper encapsulation to protect the device from environmental changes [105, 110]. Recently, Ling Xiang et al. investigated detailed requirements for the encapsulation process and encapsulant materials to meet external challenges like temperature, oxygen, moisture, and UV light [111]. Figure 6 shows the schematic of the encapsulation of commercial silicon and perovskite solar cells. Ethylene-vinyl-acetate (EVA) is the most commonly used encapsulation material for commercial use owing to its low cost, adequate transparency, and flexibility. But it is prone to acetic acid formation and has a high water vapor transmission rate. Two alternatives for EVA are thermoplastic polyolefin (TPO) and polyvinyl butyral (PVB) [112]. More recently, interest in polyolefin elastomer-based (POE) and thermoplastic polyurethane (TPU) is increasing. A variety of encapsulation materials, such as fluoropolymeric coatings, TPU, ethylene methyl acrylate, cyclized perfluoro-polymer (Cytop), organic-inorganic hybrid materials (ORMOCERs), ORMOSIL aero-gel thin film, various polymer films, etc., have been reported for perovskite solar cells [113]. Although the encapsulation method has been successfully implemented using a glass cover and inert epoxy resin, it influences the performance of the device [114, 115]. Therefore, optimization of sealing is necessary to have good performance under heat and pressure stresses. Earlier, Yaoguang Rong et al. reported that the methacrylate glue, krypton polymer layer encapsulation, etc., exhibit the stable performance of the devices for more than 1300 hours in dark conditions [114]. This type of encapsulation has been adopted by several researchers for achieving a significantly higher device operation lifetime. The performance of $MAPbI_3$ perovskite solar cells under various atmospheric conditions is described in Table 9 [36, 116 – 120].

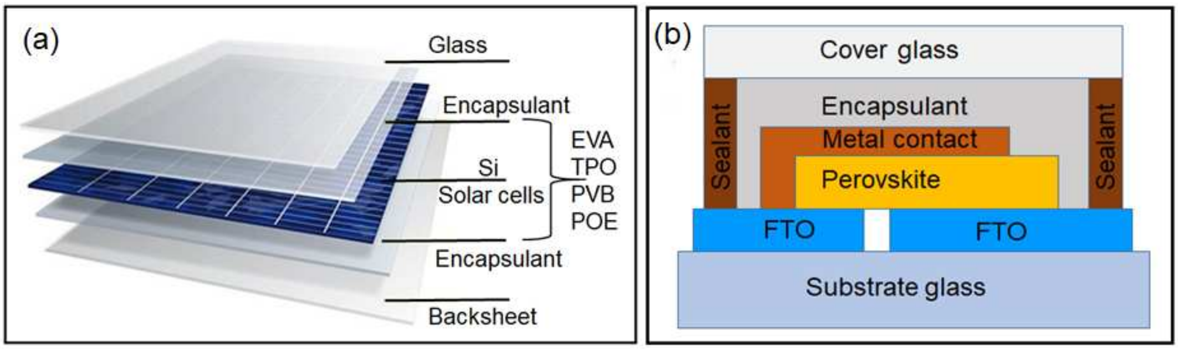

Figure 6. Encapsulation of solar cells. (a) commercial Si solar cells, (b) perovskite solar cells.

Table 9. Stability and Performance of $MAPbI_3$ perovskite solar cells in Response to Illumination, Atmospheric Conditions, and Encapsulation.

Solar Cell Structure		Testing Conditions					
	Stability Time (hours)	Illumination Dark/Light	Temperature (^{0}C)	Atmospheric Condition Humidity (%)	Encapsulation	Percentage of initial Performance (%)	Ref.
m-TiO2/**MAPbI3**/Carbon	>2000	Dark	RT	Air	No	100	[117]
m-TiO2/**MAPbI3**/PDPPDBTE/Au	1000	Dark	RT	Air (20)	No	100	[118]
ITO/NiOx/**MAPbI3**/ZnO/Al	1440	Dark	25	Air (30–35)	No	90	[119]
ITO/PETOD:PSS/**MAPbI3**/ZnO/Ag	1000	Dark	30	Air (65)	Yes	>95	[119]
m-TiO2 /ZrO2/**MAPbI3**/Carbon	>3000	Dark	RT	Air (35)	no	~100	[116]
m-TiO2/**MAPbI3**/Carbon	1002	Ultraviolet	40	Air (45)	Yes	~100	[120]
BaSnO3/**MaPbI3**/NiO/Au	1000	Light	RT	Air	Yes	93	[36]

(Light: subjected to continuous solar illumination; Dark: storage without illumination).

5.4. Alternatives to the Toxic Heavy Metal Lead

Among all perovskite materials, $MAPbI_3$ has a stable perovskite phase in air. Therefore, many researchers have focused on the optimization of this material [121, 122]. However, lead in perovskite solar cells poses serious risks to human health and the ecosystem. Ren et al. (2021) examined the latest developments in the safety issue of lead perovskite PVs and the corresponding solutions [123]. When the perovskite solar cells are degraded or damaged, the released or leaked PbI_2 pollutes the surrounding environment, exhibits toxicity toward the human respiratory and nervous systems, and increases oxidative stress [124]. Lead contamination is largely minimized in many developed countries, but the threat continues in developing countries. Nevertheless, the use of Pb in PV solar cells is likely to continue as the solar panels are pardoned from the European Legislation Restriction of Hazardous Substances [125]. The power conversion efficiency and stability of PCS cells are far better than those of lead-free PSCs. As a result, Chun-Hao Chen et al. in 2023 proposed the methodology of reducing lead leakage based on polymer resin protective layers and self-healing encapsulation, which can increase lead capture rates up to 95% under harsh conditions [126]. In summary, the development of Pb-free perovskite materials that are more competent, economical, and long-lasting may be the better option and is necessary.

Future Perovskite Materials - Machine Learning Approach

Recently, the use of computational methods and artificial intelligence (AI), referred to as machine learning (ML), has attracted worldwide attention for the prediction and assessment of perovskite materials [127]. ML is a statistical model that requires a systematic approach to data analysis based on historical data, mathematical calculations, statistics, and computer and engineering knowledge. To maintain the stability of the hybrid perovskite $MAPbI_3$, Hartono et al. (2020) developed 21 different capping layers using the ML approach [128]. Photocurrent extraction by solar cells depends on their mobility, lifetime diffusion length, and charge carriers. Consequently, researchers examined the problem via an AI approach. They proposed that this process not only facilitated the fast screening and completed the calculations of charge carrier mobilities but also provided a straightforward path to determine the charge carrier masses, electron-phonon coupling, and phonon frequency in metal halide perovskites [129].

Currently, ML and AI techniques are widely used to understand the bandgap, stability, crystal formation, and charge carrier mobilities of perovskites. These studies are limited to small structures and are considerably away from realistic conditions, such as temperature dependence, atmospheric moisture that affects the bandgap, effective masses, thermal disorders, and structural changes [130, 131]. The theoretical calculations demand a highly precise explanation of metal halide perovskites in spin-orbit coupling, interactions of charge carriers, structural properties, lattice vibrations, and the complexity of the bandgaps of hybrid and inorganic perovskite materials.

5.5. Manufacturing Cost

The affordability of any electronic device relies on its performance and long lifespan. The cost-performance ratio is calculated based on the expenses incurred regarding the raw materials used, fabrication of the device, labor, operation, overhead cost, and disposal or recycling. These factors together constitute the capital cost, which must be taken into consideration during the commercialization of the product. Although no standard lifetime has been reported for perovskites, it is assumed to be >1000 hours and needs to be further improved. Other constituents that added to the cost were the back-contact electrodes made of gold or silver. These are costly metals, and hence, it is necessary to develop economical contact materials. Alternatively, the use of highly stable carbon electrodes may reduce expenses and improve stability [116]. Copper electrodes could also be considered as an alternative in high-performance solar perovskites [132]. In addition to these issues, the main concern is the presence of lead halide in the perovskites. To minimize lead toxicity in the environment, recycling and reuse of lead (Pb) are recommended. However, recycling is economical only when there is a large active market [133, 134]. Furthermore, the conductive glass (FTO) used in solar cells is the most expensive part, which can be reused without reducing the performance of the devices.

Panel Cost Analysis

A recent report by Mark Hutchins stated the scientists came up with the new measurements that projected the production of 100 MW of perovskites solar cells [135]. The report also claims that many different viable possibilities exist to commercialize the product. Recently, Pavel Culík et al. in 2022 showed that the production of perovskite solar panels requires a process cost calculation model that includes different climate conditions and labor costs at different locations for installations [136]. They showed that perovskite PV production is competitive with other PV technologies even at smaller scales of production.

6. Conclusions

We analyzed the challenges like material and structural stability, device stability under high temperatures and humidity, lifetime, manufacturing cost, etc. faced in the commercialization of perovskite devices. Perovskite materials are highly practical and competitive for fabrication due to their benefits, such as low cost, easy fabrication technique, and perfect crystallinity. Particularly, hybrid perovskites have many advantages, such as a strong absorption coefficient, balanced mobility of the charge carriers, and small defect formation. As the power conversion efficiency and stability of PCS cells are far better than those of lead-free PSCs, the use of Pb in PV solar cells is likely to continue in the future. But the toxicity and environmental issues related to Pb in perovskite materials are of serious concerns and need to be addressed urgently before the large-scale adoption of perovskite solar panels. Therefore, to prevent mitigation of the environment and harm to human health, the proposed options are to increase the material stability, have a long lifetime of the device, use hermetic encapsulation, have a proper disposal option, and recycle the dead devices. Nonetheless, the degradation of perovskite solar cells due to prolonged exposure to high temperatures and relative humidity could not be avoided in practical applications.

The replacement of Pb metal completely from the perovskite by new non-toxic materials that possess properties like those of lead-based perovskites is necessary. Prolonged exposure of Pb may be hazardous to human health and may cause irritation to the skin, lungs, and eyes. Continuous exposure may result in serious health issues. Many materials such as Sn, Ge, Sb, Bi, etc. have so far been proposed to replace the Pb in perovskites to prevent damage to the environment.

The cost analysis shows that material selection, production, and ground installation reduce the cost significantly. The energy payback time shows the perovskite layer consumes only 1% of the input energy, and the production process consumes 5.3%. The sensitivity measurements show the major cost concerns are production, maintenance, and local labor. Here we suggest the installation of solar panels should be at a 365-day location with hot and dry weather conditions, with local maintenance and local labor such as cleaning the panel using a robot machine.

Future perovskite materials with precise knowledge about their properties are likely to be synthesized using ML and AI techniques. The compounds identified via computational methods, such as double halide perovskites and chalcogenide perovskites, have a long way to go to dominate the market because they must follow the appropriate synthesis route, deposition of thin films, device engineering, and thermodynamic stability. Computational research has suggested that double-halide perovskites and chalcogenide compounds could be reasonable replacements for the Pb metal.

The development of solar cells that are cost-effective, efficient, and stable is necessary so that they are easily widespread and accessible to the general population. In summarizing, it is suggested that the efficacious replacement of Pb metal, environmental concerns, cost-effectiveness, and industrialization challenges are required to be addressed for the widespread acceptance of perovskite solar cells.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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