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REVIEW ARTICLE

Lead–Free Perovskite Solar Cells: A Review

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ABSTRACT: Metal halide-based perovskites (ABX_3) have garnered significant attention since 2012 due to their potential to revolutionize the photovoltaic industry, surpassing the performance of traditional silicon solar cells. However, the presence of lead in these materials has raised serious environmental toxicity concerns, hindering their commercial scalability. This limitation has prompted extensive research into lead-free perovskite solar cells (PSCs), which offer a sustainable alternative despite their relatively lower power conversion efficiencies (PCE). Lead-free PSCs leverage materials such as tin (Sn), germanium (Ge), and bismuth (Bi) to achieve non-toxic and environmentally friendly solar cells. Among these, Sn-based perovskites like $MASnI_3$, $FASnI_3$, and $CsSnI_3$ have shown promise due to their direct bandgaps and eco-friendly degradation products, though their PCE is limited by factors such as heavy p-type doping. Germanium-based perovskites, though less efficient due to wider bandgaps, have shown potential when alloyed with other elements. Double halide perovskites ($A_2M^+M^{3+}X_6$), particularly Bi-based materials, offer improved stability but struggle with low carrier mobility and transport. Device architecture plays a critical role in enhancing the performance of lead-free PSCs, with inverted planar structures (p-i-n) demonstrating superior stability and charge transport efficiency compared to traditional mesoporous configurations. This review highlights the key advances, limitations, and future directions in lead-free PSC research, emphasizing the need for continued innovation in material development, device engineering, and encapsulation techniques to pave the way for environmentally sustainable and efficient solar energy solutions.

Keywords: Lead-free perovskite solar cells, Tin-based halide perovskites, Germanium-based perovskites, Double halide perovskites, Solar cell device architecture.

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1. INTRODUCTION

The global energy demand continues to surge, driven by population growth, technological advancements, and the expanding industrial sector. Electricity plays a pivotal role in modern life, serving as a foundation for domestic, industrial, and infrastructural development. However, meeting this growing demand has historically relied on conventional energy sources such as coal, natural gas, and other fossil fuels. This reliance has led to the depletion of finite natural resources and contributed significantly to environmental degradation, including greenhouse gas emissions and air pollution [1, 2]. The pressing challenges of climate change and resource scarcity necessitate a shift toward sustainable and environmentally friendly energy alternatives.

Among the plethora of renewable energy sources, solar energy stands out due to its abundance, accessibility, and clean nature. The sun provides an almost inexhaustible supply of energy, with the potential to meet global electricity needs several times over if harnessed effectively. This realization has fueled significant advancements in the field of photovoltaics, a technology that directly converts sunlight into electricity [3, 4]. Over the decades, photovoltaics has evolved to incorporate a variety of materials and structures aimed at improving efficiency, reducing costs, and enhancing scalability.

Initially, silicon-based solar cells dominated the photovoltaics landscape. Silicon solar cells, known as the first generation of photovoltaic technology, offered high efficiency and stability, becoming the industry standard. However, their production involves energy-intensive processes and high material costs, which limit their affordability for widespread adoption, especially in developing regions. This has prompted researchers to explore

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alternative materials and technologies capable of achieving comparable or superior performance at reduced costs.

In recent years, perovskite solar cells (PSCs) have emerged as a revolutionary advancement in the field of photovoltaics. These third-generation solar cells have garnered global attention due to their remarkable power conversion efficiencies (PCEs), ease of fabrication, and potential for low-cost production [5]. The perovskite structure, typically described by the chemical formula ABX_3, consists of an organic or inorganic cation (A), a divalent metal cation (B), and a halide anion (X). This unique structure imparts exceptional optoelectronic properties, including high absorption coefficients, long carrier diffusion lengths, and tunable bandgaps, making perovskites highly suitable for photovoltaic applications.

The rapid advancements in PSC technology have been extraordinary. Since their inception, PSCs have demonstrated an unprecedented rise in efficiency, rivaling and even surpassing established technologies such as cadmium telluride (CdTe) and silicon-based solar cells. As of now, PSCs have achieved a certified PCE of over 25%, underscoring their potential to revolutionize the solar energy industry [6].

Despite these remarkable achievements, the widespread adoption of lead-based PSCs faces two critical challenges: environmental and health concerns associated with lead toxicity and the material's intrinsic instability under environmental stressors such as moisture and humidity. Addressing these limitations is paramount to ensuring the long-term viability and commercialization of PSC technology [7].

2. LIMITATIONS OF LEAD HALIDE (ABX_3) PEROVSKITE SOLAR CELLS

Lead-based perovskites possess nearly ideal optoelectronic properties for photovoltaic applications. Their narrow bandgap, high optical absorption coefficients, long carrier lifetimes, and high mobilities contribute to their exceptional efficiency. However, their reliance on lead, a toxic heavy metal, raises significant environmental and health concerns. Lead contamination poses severe risks to ecosystems and human health, necessitating stringent handling and disposal protocols. Additionally, the degradation of lead-based perovskites can result in the leaching of lead into the environment, further exacerbating these concerns. Beyond toxicity, the stability of lead-based PSCs remains a critical issue. These materials are highly sensitive to moisture, oxygen, and thermal fluctuations, leading to rapid degradation and loss of efficiency over time. This vulnerability to environmental factors poses significant challenges for their deployment in real-world conditions, where long-term operational stability is essential [8].

Efforts to address the toxicity issue have spurred extensive research into lead-free alternatives. Ideal lead-free perovskites should exhibit comparable or superior properties to their lead-based counterparts, including narrow bandgaps, high absorption coefficients, high charge carrier mobilities, and low exciton binding energies. Among the emerging candidates, tin (Sn), germanium (Ge), bismuth (Bi), and antimony (Sb)-based perovskites have shown promise. These materials are being actively explored for their potential to achieve high efficiency while eliminating the environmental and health risks associated with lead [9].

Simultaneously, strategies to enhance the stability of perovskites have focused on advanced encapsulation techniques, compositional engineering, and the development of hybrid structures. Encapsulation involves protective layers that shield the perovskite material from environmental factors, thereby prolonging its operational lifespan [10]. Compositional engineering, on the other hand, involves modifying the perovskite's chemical structure to improve its intrinsic stability without compromising performance. Hybrid structures, which combine perovskites with other materials, are also being explored to achieve synergistic improvements in stability and efficiency [11]. The development of lead-free perovskites represents a significant step toward realizing sustainable and eco-friendly photovoltaic technology. These alternatives not only address the environmental concerns associated with lead but also open new avenues for innovation in materials science and device engineering. As research progresses, the integration of lead-free perovskites with scalable fabrication techniques and advanced encapsulation methods holds the promise of ushering in a new era of high-performance, environmentally benign solar cells [12].

3. TIN (Sn) BASED HALIDE PEROVSKITES

Tin (Sn) based halide perovskites, including Methylammonium Tin Iodide ($MASnI_3$), Formadinium Tin Iodide ($FASnI_3$), and Cesium Tin Halide ($CsSnI_3$), have garnered significant attention as promising alternatives to their lead-based counterparts in the field of perovskite solar cells. These materials not only offer comparable optoelectronic properties to lead-based perovskites but also stand out due to their potential for lower environmental toxicity, making them more suitable for sustainable applications. The fundamental appeal of Sn-based halide perovskites lies in their direct bandgaps, which range around 1.2 eV for $MASnI_3$, 1.4 eV for $FASnI_3$, and 1.3 eV for $CsSnI_3$. These bandgaps fall in the optimal range for high-efficiency solar energy conversion, similar to their lead counterparts ($APbX_3$), yet without the environmental hazards associated with lead [13].

However, Sn-based perovskites present unique challenges. One major issue is the degradation upon exposure to air, where Sn^{2+} ions oxidize to form Sn^{4+} ions, leading to the formation of tin oxide (SnO_2), a relatively eco-friendly material. This air-sensitive degradation process severely impacts the stability and long-term performance of Sn-based perovskites, a challenge that must be addressed for practical

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applications in solar cells and other optoelectronic devices [14].

Recently, researchers made significant strides in harnessing Sn-based perovskites as absorber materials for solid-state solar cells [15]. In their pioneering work, they used Methylammonium Tin Iodide ($CH_3NH_3SnI_3$) as the absorber material in conjunction with the hole transport layer Spiro-OMeTAD [16]. This configuration resulted in an absorption onset at approximately 950 nm, marking a promising achievement in Sn-based perovskite solar cells. Further modifications to the material, such as chemical treatment with a bromide precursor, led to an improvement in the power conversion efficiency (PCE) to 5.8%. The ability to vary the doping level in Sn-based perovskites also contributed to the material's versatility, with carrier concentrations as high as $1x10^{19}$ cm^{-3} [17].

Despite these advancements, Sn-based perovskites still face significant challenges when compared to their lead-based analogs. To date, the highest reported PCE for Sn-based perovskites is around 10%, which is still much lower than the PCEs achieved by lead-based perovskites. A major factor contributing to this lower performance is the low open-circuit voltage (V_{oc}) observed in Sn-based perovskites, which typically ranges around 0.5 V [18]. This value is notably lower than that of lead-based perovskites, where V_{oc} values above 1 V are commonly achieved. One hypothesis for this low V_{oc} is the extensive p-type doping in Sn-based perovskites, which leads to increased recombination of photogenerated charge carriers, thereby reducing the overall performance of the device. The current density (J_{sc}) of Sn-based perovskites typically falls between 20 and 25 mA/cm^2, a value that is competitive but still less than the performance of high-efficiency lead-based perovskite solar cells [19].

The crystal structure of Sn-based perovskites also plays a crucial role in determining their optoelectronic properties. Like other perovskites, Sn-based perovskites adopt the ABX_3 crystal structure, where A is a large cation (often organic), B is a smaller metal cation (in this case, tin or another divalent metal like germanium), and X is a halogen atom as shown in Figure 1. The arrangement of these ions is sensitive to temperature, pressure, and the tolerance factor, which is a critical parameter influencing the stability of the perovskite structure. The tolerance factor, denoted as *t*, is given by the equation:

$$t = \frac{rA+rB}{\sqrt{2}(rB-rX)} \quad (1)$$

Where *rA*, *rB*, and *rX* represent the ionic radii of the A cation, B cation, and X halogen ion, respectively [20]. The stability of the crystal structure is highly dependent on the value of this tolerance factor, which governs whether the structure adopts an orthorhombic, tetragonal, or cubic phase. For Sn-based perovskites, the optimal tolerance factor ensures a stable crystal arrangement that maximizes efficiency and minimizes defects [21].

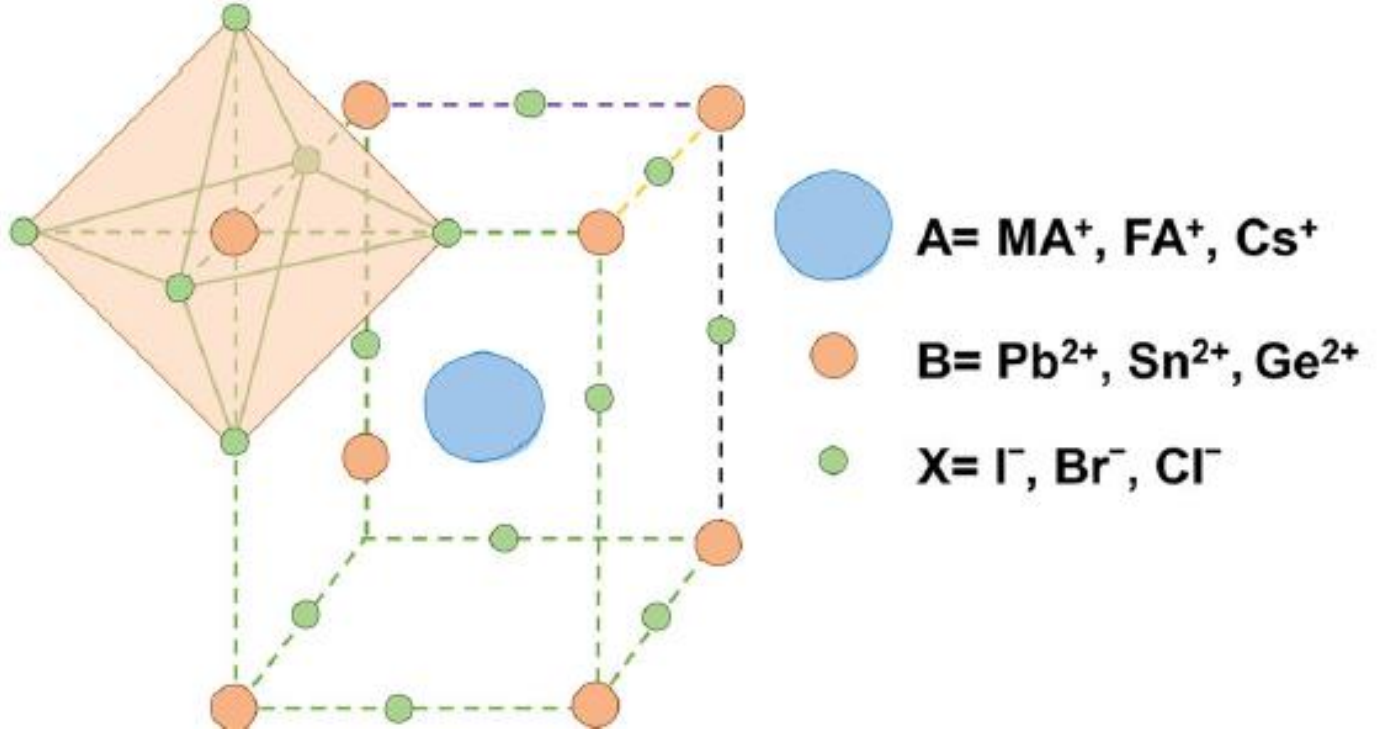

Fig. 1. Crystal structure of 3D perovskite. Reprinted with permission from ref. [**16**], Aktas, E., Rajamanickam, N., Pascual, J., Hu, S., Aldamasy, M.H., Di Girolamo, D., Li, W., Nasti, G., Martínez-Ferrero, E., Wakamiya, A. and Palomares, E., **2022.** Challenges and strategies toward long-term stability of lead-free tin-based perovskite solar cells. *Communications Materials*, *3*(1), p.104. Copyright © Springer Nature.

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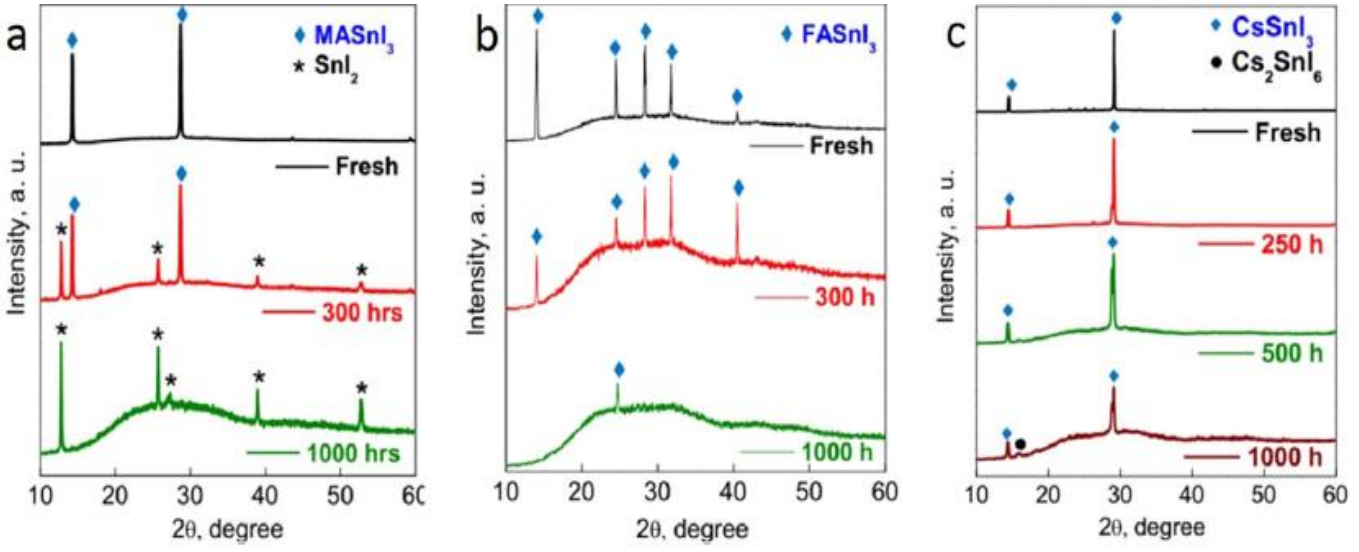

Fig. 2. XRD patterns of (a) $MASnI_3$, (b) $FASnI_3$, and (c) $CsSnI_3$. Reprinted with permission from ref. [**16**], Aktas, E., Rajamanickam, N., Pascual, J., Hu, S., Aldamasy, M.H., Di Girolamo, D., Li, W., Nasti, G., Martínez-Ferrero, E., Wakamiya, A. and Palomares, E., **2022.** Challenges and strategies toward long-term stability of lead-free tin-based perovskite solar cells. *Communications Materials*, *3*(1), p.104. Copyright © Springer Nature.

Research by Akbulatov and colleagues has provided insights into the thermal and photochemical stability of various Sn-based perovskites, including $MASnI_3$, $FASnI_3$, and $CsSnI_3$. Their study involved annealing these materials at 90°C and evaluating their X-ray diffraction (XRD) patterns as shown in Figure 2 [16]. The results showed that $CsSnI_3$ exhibited remarkable thermal stability, maintaining its structure even after 1000 hours of exposure to elevated temperatures. However, the material also showed signs of impurity formation, particularly the presence of Cs_2SnI_6, which was evident in the XRD patterns [22]. Cs_2SnI_6 is a relatively stable form of Sn-based perovskite that contains Sn^{4+} ions but does not fully adopt the perovskite structure. This material has a direct bandgap ranging from 1.3 to 1.6 eV, but its low carrier mobility and short diffusion lengths limit its efficiency in photovoltaic applications. The key to improving the performance of $CsSnI_3$ and similar materials lies in developing methods to fabricate films with larger grain sizes and fewer structural defects, which would reduce carrier recombination and enhance device performance [23].

The potential of Sn-based perovskites for high-efficiency, lead-free solar cells is clear, but significant hurdles remain in terms of stability, efficiency, and scalability. Advances in material design, processing techniques, and understanding of the underlying physics of Sn-based perovskites will be crucial in overcoming these challenges. By addressing issues related to degradation, optimizing doping levels, and enhancing the crystallinity of these materials, Sn-based perovskites could one day become a viable and environmentally friendly alternative to lead-based perovskites for solar energy harvesting [24].

4. GERMANIUM (Ge)-BASED HALIDE PEROVSKITES

Germanium (Ge)-based halide perovskites have been a subject of interest due to their potential as a lead-free alternative to traditional lead-based perovskites. However, these materials face significant challenges in terms of performance, which has hindered their widespread application, particularly in solar cell technologies. Compared to their lead (Pb)-based and tin (Sn)-based analogs, Ge-based perovskites generally exhibit inferior performance. One key issue is their bandgap characteristics. For instance, $CsGeI_3$, a common Ge-based perovskite, has a relatively narrow bandgap of about 1.6 eV, which is suitable for solar cell applications. However, other Ge-based perovskites, such as Methylammonium Germanium Iodide ($MAGeI_3$) and Formamidinium Germanium Iodide ($FAGeI_3$), have wider bandgaps of around 1.9 eV and 2.2 eV, respectively. These wider bandgaps are less favorable for solar cell applications as they do not absorb light in the optimal wavelength range for energy conversion [25]. **Figure 3** shows the SEM image of Ge-based device.

Despite these challenges, Ge-based perovskites and their alloys show promise when combined with other materials. Ge-containing alloys, for example, can be more efficient than pure Ge-based perovskites when used as absorber layers in solar cells. A notable example is the $CsSn_{0.5}Ge_{0.5}I_3$ alloy, which combines tin (Sn) and germanium (Ge) to create a material with a narrower bandgap of 1.5 eV. This alloy has demonstrated a power conversion efficiency (PCE) of 7.11%, which is a significant improvement over

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pure Ge-based perovskite [26]. When processed using the thermal evaporation method, the $CsSn_{0.5}Ge_{0.5}I_3$ film maintained 92% of its original efficiency for approximately 500 hours without encapsulation, indicating its potential for relatively long-term stability in photovoltaic applications [27].

In another study, a solar cell device was constructed with a Glass/ITO/PEDOT: PSS/$MAGeI_{2.7}$ $Br_{0.3}$/$PC_{70}BM$/Ag architecture, where $MAGeI_{2.7}Br_{0.3}$ is a germanium-based perovskite material. The device's performance was analyzed using various techniques, including scanning electron microscopy (SEM), current-voltage (J-V) measurements, and external quantum efficiency (EQE) spectra. The SEM image (Figure 4A) showed the distinct layer structure of the device, where each material was stacked in a well-defined manner. The J-V curves measured under dark and light conditions (Figure 4B) revealed a voltage at open circuit (V_{oc}) of 460 mV, a short-circuit current density (J_{sc}) of 3.11 mA/cm², a PCE of 0.68%, and a fill factor of 0.48. While these values are modest, they reflect the potential of germanium-based perovskite devices, particularly when combined with other materials like $PC_{70}BM$. The EQE spectra (Figure 4C) showed a response below 500 nm, consistent with the expected absorption characteristics of Ge-based perovskite devices, providing further evidence of the material's potential [28].

Although Ge-based perovskites are not yet as efficient as Pb-based perovskites, research into their alloys and device structures continues to make progress. **Figure 4** shows the device architecture and energy band diagram of Sn/Ge based perovskite by optimizing the composition of these materials and exploring different device architectures, Ge-based halide perovskites may eventually become competitive alternatives to lead-based perovskites in solar energy applications. For now, their relatively narrow bandgaps, coupled with improved stability in certain configurations, suggest that they have a promising future in the field of renewable energy. However, further improvements in performance and long-term stability are crucial for their commercialization and widespread adoption [25].

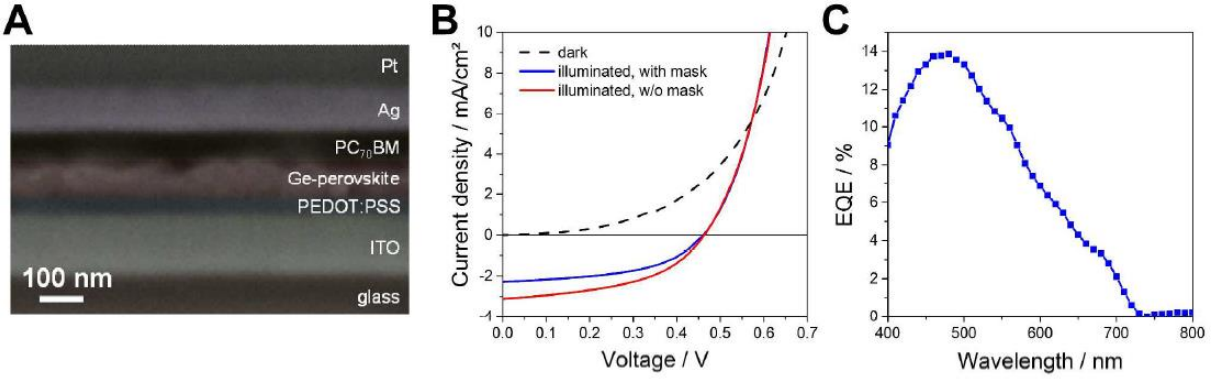

Fig. 3. (A) SEM image of Ge-based device, (B) J-V curve of device, (C) EQE spectra of Ge-based device. Reprinted with permission from ref. [25], Kopacic, I., Friesenbichler, B., Hoefler, S.F., Kunert, B., Plank, H., Rath, T. and Trimmel, G., **2018.** Enhanced performance of germanium halide perovskite solar cells through compositional engineering. *ACS Applied Energy Materials*, *1*(2), pp.343-347. Copyright © American Chemical Society.

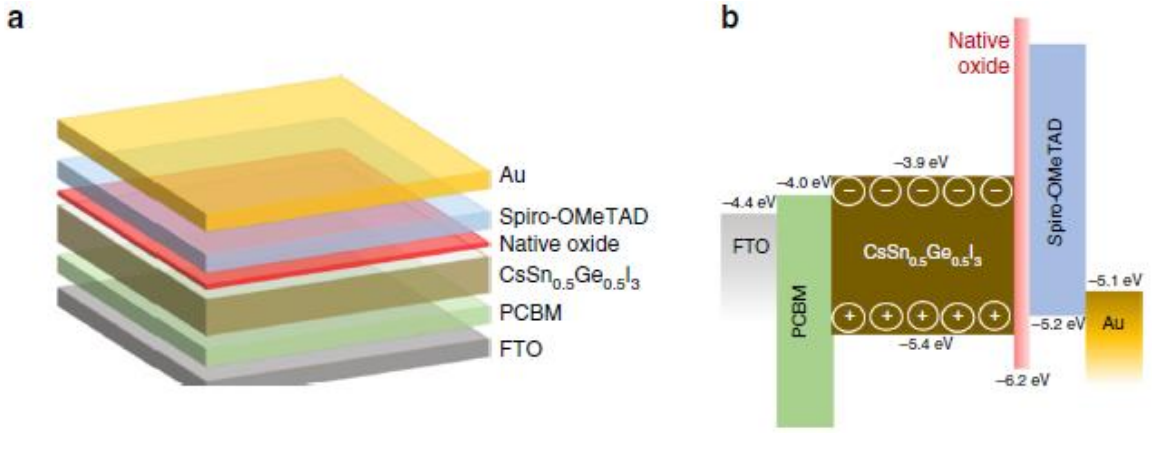

Fig. 4. (a) Device architecture of Sn/Ge-based perovskite, and (b) Energy Band diagram of (a). Reprinted with permission from ref. [29], Chen, M., Ju, M.G., Garces, H.F., Carl, A.D., Ono, L.K., Hawash, Z., Zhang, Y., Shen, T., Qi, Y., Grimm, R.L. and Pacifici, D., **2019.** Highly stable and efficient all-inorganic lead-free perovskite solar cells with native-oxide passivation. *Nature Communications*, *10*(1), p.16. Copyright © Springer Nature.

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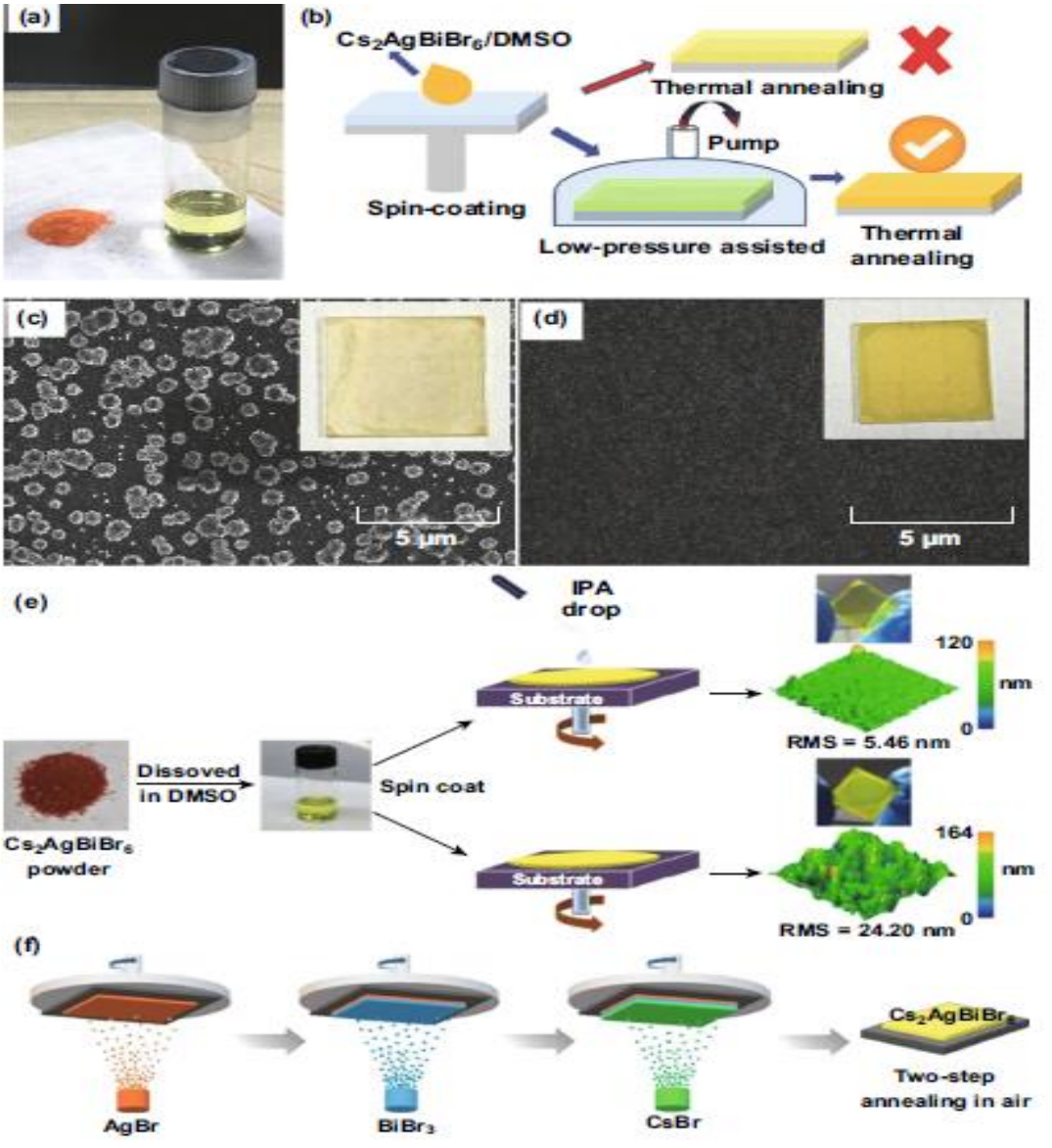

Fig. 5. (a) $Cs_2AgBiBr_6$ powder, (b) Thin film fabrication methodology, (c, d) SEM images of obtained film, (e) Schematic of the spin coating process, and (f) Sequential of vapor deposition processing. Reprinted with permission from ref. [30], Chu, L., Ahmad, W., Liu, W., Yang, J., Zhang, R., Sun, Y., Yang, J. and Li, X.A., **2019.** Lead-free halide double perovskite materials: a new superstar toward green and stable optoelectronic applications. *Nano-Micro Letters*, *11*, pp.1-18. Copyright © Springer Nature.

5. DOUBLE HALIDE PEROVSKITE MATERIALS

In addition to tin (Sn) and germanium (Ge) based halide perovskites, double halide perovskite materials have emerged as an exciting alternative in the quest for efficient, stable, and environmentally friendly materials for optoelectronic applications, including solar cells. These materials typically have a chemical formula of $A_2M^+M^{3+}X_6$, where A is an organic or inorganic cation, M^+ is a monovalent cation, M^{3+} is a trivalent cation, and X represents a halide anion. Double halide perovskites have been of significant interest due to their unique structural characteristics, higher stability, and potential for use in various optoelectronic devices [30].

Figure 5 shows the fabrication methodology of $Cs_2AgBiBr_6$ double perovskite. One of the key advantages of double halide perovskites is their wider bandgap, typically around 2 eV, which is advantageous for applications in solar cells. A wider bandgap allows for better absorption of higher-energy photons, and in the case of perovskite solar cells, it is believed that a wider bandgap can improve the device's ability to absorb light and efficiently convert solar energy. This wider bandgap also helps in enhancing the stability of the material, which is a significant concern for perovskite-based devices. Stability is a major issue for traditional perovskites, especially lead-based ones, which degrade upon exposure to moisture and oxygen. Double halide perovskites, due to their

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stronger chemical bonds and higher lattice stability, tend to exhibit better resistance to environmental degradation, making them more promising for long-term applications in solar energy devices [31].

However, despite these promising characteristics, double halide perovskites also face several challenges that prevent them from reaching their full potential. One of the key limitations of these materials is their low carrier mobilities. Carrier mobility is an important factor in determining the efficiency of a material in optoelectronic devices, particularly in solar cells, where high carrier mobility can lead to faster charge transport, reduced recombination, and improved device performance. In the case of double halide perovskites, the carrier mobility is often insufficient for high-efficiency device operation, leading to lower overall performance in solar cells. This limitation is largely due to the structural characteristics of these materials, which can lead to scattering and trapping of charge carriers, hindering their ability to efficiently transport charge.

Moreover, low carrier transport further limits the efficiency of devices made from these materials. Efficient carrier transport is essential for minimizing losses in solar cells, as it ensures that the photogenerated charge carriers can reach the electrode interfaces without recombining. For double halide perovskites, the weak interaction between the layers of the crystal structure can create barriers for charge carriers, resulting in poor transport and reduced performance. This is particularly problematic when designing devices such as solar cells, where the rapid movement of electrons and holes to their respective electrodes is crucial for achieving high efficiency [32, 33].

Bismuth (Bi)-based perovskites are one of the prominent types of double halide perovskites, and they have attracted considerable attention due to their non-toxic nature and potential for use in lead-free devices. However, despite their promising environmental benefits, Bi-based perovskites have not yet demonstrated the high efficiencies seen in other perovskite materials [34]. These materials fall into a similar category as Cs_2SnI_6 perovskites, which, while stable, still suffer from low efficiency and carrier mobility issues [35]. Bismuth-based perovskites, including $Cs_3Bi_2I_9$ and other similar compounds, have shown relatively low power conversion efficiencies (PCE) due to their poor charge transport and suboptimal absorption properties. These materials often exhibit low current densities (J_{sc}), which significantly impacts their ability to function as effective absorbers in solar cells. As a result, Bi-based perovskites have not yet reached the performance levels of lead or tin-based perovskites, and their efficiency remains lower in comparison.

For example, solar cells made with $Cs_3Sb_2I_9$, a double halide perovskite composed of antimony, show low J_{sc} values, which limit their efficiency as absorbers in solar cells. This material exhibits poor charge extraction, which results in low photocurrent generation and overall low performance in photovoltaic devices. While the material is stable and non-toxic, its inability to efficiently transport charge carriers and absorb light limits its practical applications.

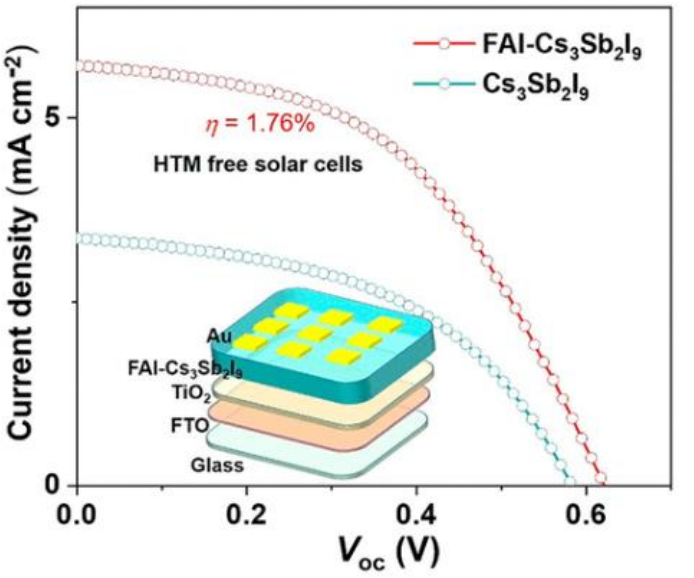

Fig. 6. J-V curve of FAI- $Cs_3Sb_2I_9$ perovskite. Reprinted with permission from ref [37] Farooq, U., Zhang, M., Chi, D., Wang, J., Idris, A.M., Huang, S., Pan, Z. and Li, Z., 2023. Surface Defects Passivation with Organic Salt for Highly Stable and Efficient Lead-Free $Cs_3Sb_2I_9$ Perovskite Solar Cells. *ACS Applied Energy Materials*, *6*(20), pp.10294-10302. Copyright © American Chemical Society.

Despite these challenges, there is ongoing research focused on improving the performance of double halide perovskites. Various strategies are being explored, such as doping with different elements, modifying the crystal structure, and improving film processing techniques to enhance carrier mobility and light absorption. Additionally, hybrid materials combining double halide perovskites with other semiconductors or organic materials may offer pathways to overcome the limitations of low carrier mobility and transport [36].

In conclusion, double halide perovskites represent a promising class of materials for solar energy and optoelectronic applications due to their stability, wider bandgap, and potential for environmentally friendly devices. However, challenges such as low carrier mobilities and poor carrier transport must be addressed before these materials can achieve the high efficiencies required for commercial applications. Ongoing research is focused on overcoming these limitations, and improvements in material design and device engineering may unlock the full potential of double halide perovskites in future energy technologies [37]. Figure 6 shows the J-V curve of FAI- $Cs_3Sb_2I_9$ perovskite.

6. ROLE OF DEVICE ARCHITECTURE IN PEROVSKITE SOLAR CELLS

The device architecture plays a critical role in the performance and stability of perovskite solar cells, especially in the context of Sn-based perovskites. The overall efficiency

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of a perovskite solar cell depends on the optimal arrangement of layers, their respective material properties, and the interaction between them. Among the various configurations available, the mesoporous configuration (n-i-p) and planar configurations (n-i-p and p-i-n) are widely used, with each offering distinct advantages and challenges in terms of stability, efficiency, and performance [38]. Figure 7 throws light on the three types of architecture.

6.1. Mesoporous Configuration (n-i-p)

The mesoporous n-i-p (n-type, intrinsic, p-type) configuration is one of the most commonly used architectures in perovskite solar cells. In this configuration, a mesoporous layer of titanium dioxide (TiO_2) serves as the electron transport layer (ETL) and acts as a scaffold for the absorber layer. TiO_2 is an excellent material for this purpose due to its high electron mobility, good transparency, and effective charge transport properties. It facilitates efficient electron extraction from the absorber layer, ensuring that the generated charge carriers can move towards the electrode interfaces without recombination.

In the n-i-p architecture, the perovskite absorber layer is deposited on top of the mesoporous TiO_2 scaffold. The hole transport layer (HTL) is typically made of Spiro-OMeTAD, which is a widely used organic material known for its high hole mobility and compatibility with perovskite absorbers. The HTL is responsible for extracting holes (positive charge carriers) from the perovskite layer and transporting them to the top electrode. While the mesoporous n-i-p structure is widely used due to its relatively simple fabrication process and good performance with lead-based perovskites, it poses stability issues when applied to Sn-based perovskites. One of the significant challenges with Sn-based halide perovskites is their susceptibility to oxidation. The Sn^{2+} ions in the perovskite material can easily oxidize to Sn^{4+}, especially when exposed to oxygen or moisture. In the n-i-p configuration, the TiO_2 layer has been found to exacerbate this issue by promoting the oxidation of Sn^{2+} to Sn^{4+}, which leads to the degradation of the perovskite material. This results in lower performance and reduced long-term stability for Sn-based perovskite solar cells. Therefore, while the n-i-p configuration is widely used, its application in Sn-based perovskites requires careful consideration of the material compatibility and stability [39].

6.2. Planar n-i-p and p-i-n Structures

In contrast to the mesoporous configuration, planar perovskite solar cells are constructed by stacking the various layers directly on top of each other, without the use of a mesoporous scaffold. The architecture can either be n-i-p or p-i-n, depending on the orientation of the layers.

n-i-p Structure: In the planar n-i-p structure, the electron transport layer (ETL) is positioned at the bottom, followed by the intrinsic perovskite layer and the hole transport layer (HTL) at the top. This configuration is also known as a normal or conventional planar structure, where the light enters from the top and travels through the HTL, the perovskite absorber, and then to the ETL. The performance of planar n-i-p devices is highly dependent on the properties of the ETL and HTL, as well as the quality and thickness of the perovskite layer [40].

p-i-n Structure: On the other hand, the planar p-i-n configuration is inverted. In this structure, the light first interacts with the HTL, followed by the perovskite layer and the ETL at the bottom. This inverted structure has been shown to provide improved performance for Sn-based halide perovskites compared to the conventional n-i-p structure. The reason for this is that the inverted planar p-i-n configuration offers better charge transport and extraction, which is crucial for improving the voltage output (V_{oc}) and overall efficiency of Sn-based perovskite solar cells.

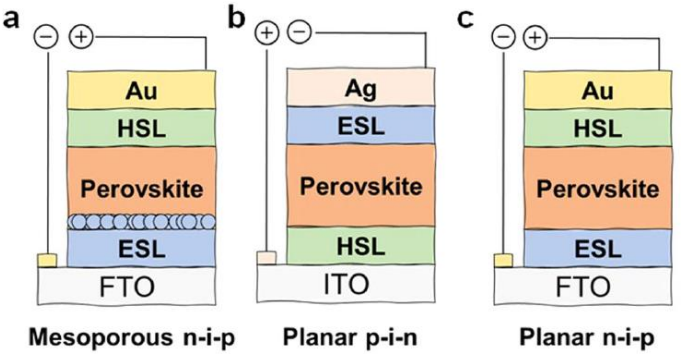

Fig. 7. (a) Mesoporous p-i-n, (b) Planar p-i-n, and (c) Planar n-i-p. Reprinted with permission from ref. [16], Aktas, E., Rajamanickam, N., Pascual, J., Hu, S., Aldamasy, M.H., Di Girolamo, D., Li, W., Nasti, G., Martínez-Ferrero, E., Wakamiya, A. and Palomares, E., **2022.** Challenges and strategies toward long-term stability of lead-free tin-based perovskite solar cells. *Communications Materials*, *3*(1), p.104. Copyright © Springer Nature.

Research has shown that one effective combination for the p-i-n structure is using PCBM (phenyl-C61-butyric acid methyl ester) as the ETL and PEDOT: PSS (Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate)) as the HTL. PCBM is an efficient electron transport material that has good compatibility with the perovskite absorber, facilitating efficient electron extraction and transport to the electrode. PEDOT: PSS, on the other hand, is an organic polymer with excellent hole transport properties, ensuring efficient hole collection from the perovskite layer. Together, this combination enhances the charge transport and extraction processes, which directly improves the V_{oc} and overall performance of the device [41].

Furthermore, the addition of a BCP (bathocuproine) hole-blocking layer has been found to significantly improve the performance of the p-i-n structure. BCP acts as a barrier

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to prevent the recombination of charge carriers, which can otherwise lead to energy losses and reduced device efficiency. By blocking the flow of holes to the ETL, BCP ensures that the holes are efficiently transported to the top electrode, resulting in enhanced charge collection, improved efficiency, and a higher V_{oc} [42].

7. BAND DIAGRAMS AND PERFORMANCE OPTIMIZATION

The band diagrams of Sn-based perovskites play an important role in understanding the charge transport and extraction processes in perovskite solar cells. As shown in the schematic of the band diagram in Figure 8, the alignment of energy levels between the perovskite absorber, ETL, and HTL is crucial for efficient charge extraction and reduced recombination. Proper alignment helps to facilitate the flow of electrons from the perovskite layer to the ETL and holes from the perovskite layer to the HTL, thereby improving the device's performance [43].

The device architecture plays a pivotal role in determining the efficiency and stability of Sn-based perovskite solar cells. While the mesoporous n-i-p configuration is widely used, it is prone to stability issues in Sn-based perovskites due to the oxidation of Sn^{2+} to Sn^{4+}. On the other hand, planar p-i-n configurations have demonstrated superior performance for Sn-based perovskites by providing improved charge transport and extraction, resulting in higher Voc and efficiency. The use of optimized ETL and HTL materials, along with additional hole-blocking layers, has been shown to further enhance device performance. As research continues, further innovations in device architecture and material design will be key to unlocking the full potential of Sn-based perovskite solar cells [44]. Figure 8 shows the Energy band diagrams of various perovskites.

8. ROLE OF CHARGE TRANSPORT LAYERS (CTLS) IN PEROVSKITE SOLAR CELLS (PSCS)

Charge transport layers (CTLs) are critical components in the functioning and efficiency of perovskite solar cells (PSCs). Their primary role is to facilitate the extraction of charge carriers—electrons and holes—generated in the perovskite absorber layer, while simultaneously suppressing non-radiative recombination. The performance of PSCs is heavily influenced by the properties and materials used for these layers. An efficient CTL not only improves the overall efficiency of the solar cell but also contributes to its long-term stability. This makes the study and optimization of CTLs a key area of research for advancing PSC technology [45]. Figure 9 shows the Energy band diagrams of various ETL and HTL materials.

8.1. Properties of Ideal Charge Transport Layers

The properties of CTLs directly affect the charge extraction efficiency and the stability of the perovskite solar cell. Several key characteristics define an ideal CTL [47]:

Energy Level Alignment: The energy levels of the CTLs must be well-matched with those of the perovskite absorber. The conduction band (for electron transport layers, ETLs) and valence band (for hole transport layers, HTLs) of the CTLs must align with the perovskite's energy levels to allow efficient charge carrier extraction. Misalignment can lead to poor charge transfer and increased recombination losses, which reduce the overall efficiency of the device.

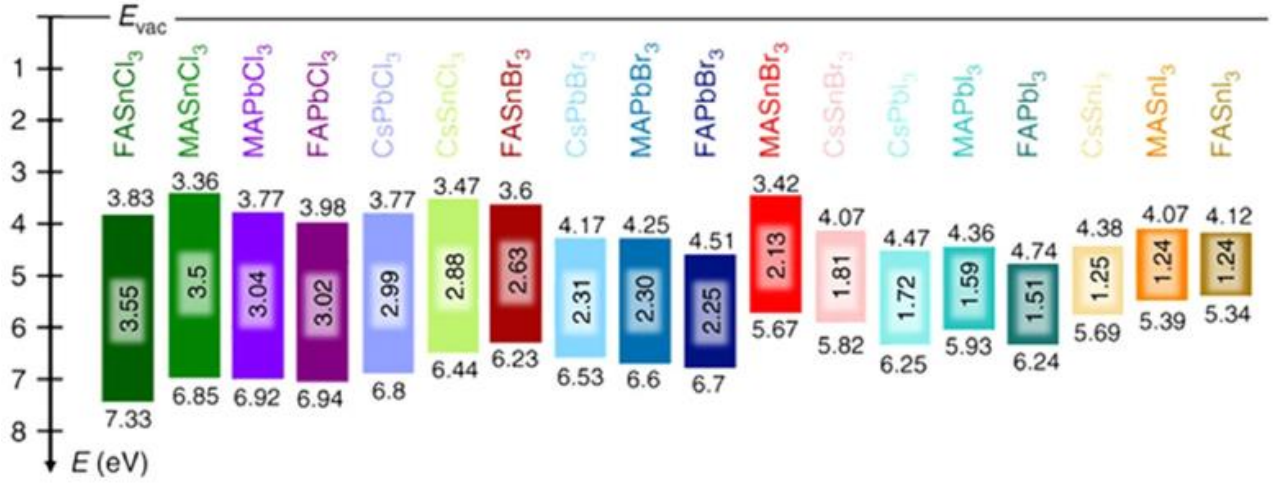

Fig. 8. Energy Band Diagrams (EBD) of different perovskites. Reprinted with permission from ref. [16], Aktas, E., Rajamanickam, N., Pascual, J., Hu, S., Aldamasy, M.H., Di Girolamo, D., Li, W., Nasti, G., Martínez-Ferrero, E., Wakamiya, A. and Palomares, E., **2022.** Challenges and strategies toward long-term stability of lead-free tin-based perovskite solar cells. *Communications Materials*, *3*(1), p.104. Copyright © Springer Nature.

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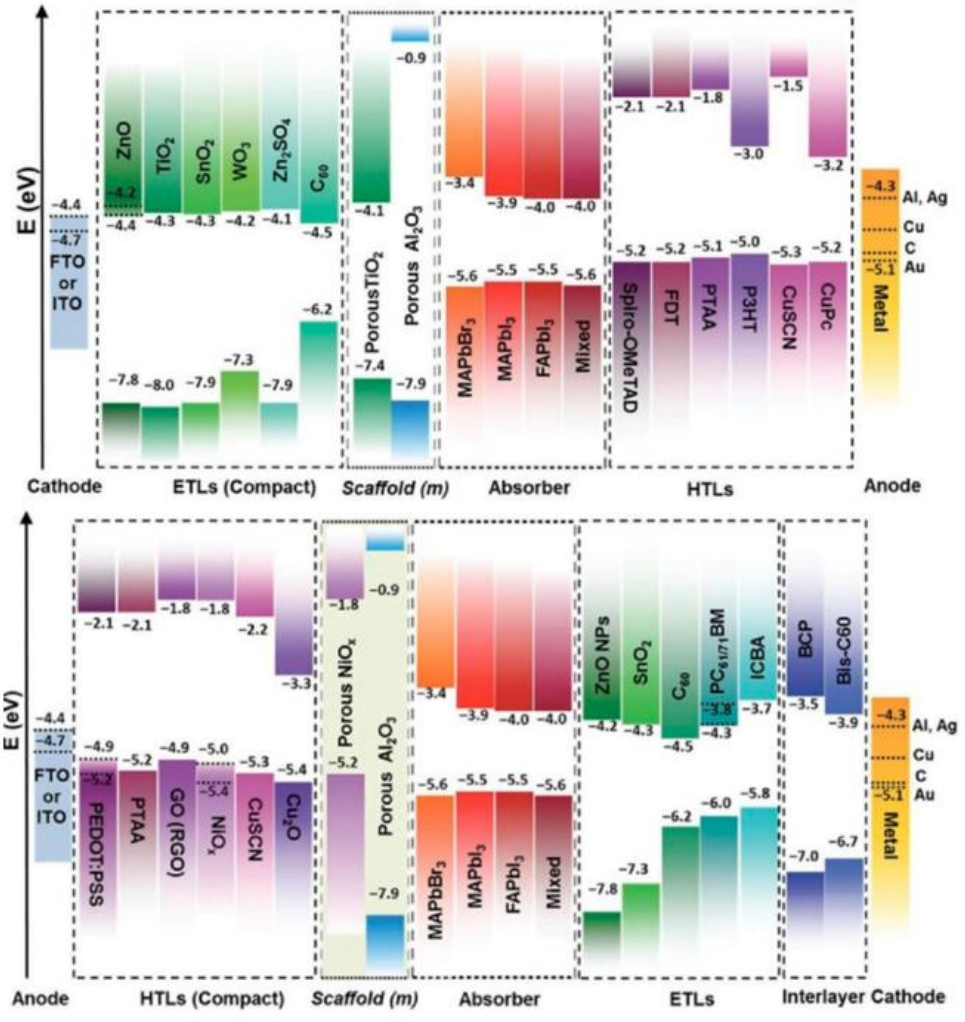

Fig. 9. Energy band diagrams of various ETL and HTL materials. Reproduced with permission from ref. [46], Chen, J. and Park, N.G., 2020. Materials and methods for interface engineering toward stable and efficient perovskite solar cells. *ACS Energy Letters*, *5*(8), pp.2742-2786.Copyright © American Chemical Society.

Transparency: To minimize energy losses, the CTL should be highly transparent, especially in the visible spectrum. This is particularly important for ETLs and HTLs, as they should allow as much light as possible to reach the perovskite layer for absorption. Any absorption in the CTL would reduce the amount of light available for charge generation, thereby decreasing the efficiency of the solar cell.

High Electron and Hole Mobility: For efficient charge transport, CTLs must exhibit high mobility for electrons (in the case of ETLs) and holes (in the case of HTLs). High mobility ensures that charge carriers are transported quickly and effectively to the respective electrodes, minimizing recombination and improving the power conversion efficiency (PCE) of the solar cell.

8.2. Common Charge Transport Layer Materials

Several materials have been investigated for use as CTLs in perovskite solar cells, each with varying degrees of effectiveness in terms of charge transport and stability [48].

Mesoporous Titanium Dioxide (TiO_2): TiO_2 is a widely used electron transport layer (ETL) material in conventional perovskite solar cells. It is favored for its excellent electron mobility, stability, and good alignment with the conduction band of many perovskite materials. Mesoporous TiO_2 is often used in combination with a mesoporous scaffold to support the perovskite absorber. However, TiO_2 can suffer from issues like fast decay due to the presence of oxygen vacancies when exposed to ultraviolet (UV) light, which can degrade the device performance over time. Additionally, TiO_2's interaction with the perovskite layer can lead to trap states, which contribute to non-radiative recombination.

Spiro-OMeTAD (Hole Transport Layer, HTL): Spiro-OMeTAD is one of the most commonly used hole transport materials in PSCs. It is a small organic molecule known for its high hole mobility and ability to facilitate efficient hole

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extraction from the perovskite absorber. Moreover, Spiro-OMeTAD has been instrumental in solving the corrosion problem that occurs when liquid electrolytes are used in the fabrication of all-solid-state perovskite solar cells. However, it is relatively expensive and requires the use of dopants like lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) for enhancing conductivity, which can introduce additional complexity in device fabrication.

Nickel Oxide (NiOx) and Zinc Oxide (ZnO): Inorganic materials such as NiOx and ZnO have shown promise as HTLs and ETLs, respectively, for stable and efficient PSCs. NiOx is a p-type material that is chemically stable and can be used in combination with n-type ETLs like ZnO to form highly efficient inverted planar (p-i-n) structures. These materials are particularly advantageous in terms of operational stability, as they are chemically inert and low-cost. NiOx-based PSCs have demonstrated air-stable performance, retaining approximately 90% of their original efficiency after 60 days of storage at room temperature, making them highly suitable for commercialization.

Fullerene-Derived Materials (PCBM and C60): Fullerene derivatives, such as PCBM and C60, have been developed as promising electron transport materials, particularly in inverted planar or p-i-n configurations. These materials are used as ETLs in combination with various HTLs, and they have shown good performance in terms of charge transport and device efficiency. Fullerenes are particularly useful in inverted structures because they facilitate efficient electron extraction from the perovskite layer and minimize recombination losses.

9. INTERFACE ENGINEERING AND TRAP STATE PASSIVATION

The interface between the charge transport layers (CTLs) and the perovskite layer plays a crucial role in the overall performance of PSCs. Imperfect interfaces often lead to the formation of trap states, which act as recombination centers and reduce the efficiency of charge collection. These trap states arise due to the incomplete or misaligned energy levels at the interface between the perovskite and the CTLs, resulting in non-radiative recombination [49].

To address this issue, significant efforts have been made to improve the interface between the CTLs and the perovskite layer. Interface modification strategies, such as the use of interfacial layers or treatments, are employed to reduce trap states and enhance charge carrier extraction. In 2014, Zhou et al. demonstrated that modifying the interface with polyethyleneimine ethoxylated (PEIE) significantly improved the electron extraction process. This modification led to a maximum power conversion efficiency (PCE) of over 19% for perovskite solar cells [46]. Figure 10 explains about the defect passivation effect by C8 at the interfaces.

Another effective strategy for improving the interface and suppressing non-radiative recombination is contact passivation. For example, treating NiOx/perovskite interfaces with alkali chloride has been shown to improve the ordering and reduce defect density at the interface, leading to enhanced device performance. By passivating the defects at the interface, these treatments effectively reduce the recombination losses and increase the efficiency and stability of the device.

Charge transport layers (CTLs) are essential components of perovskite solar cells, as they influence both the efficiency and stability of the devices. The ideal CTLs should have well-matched energy levels with the perovskite layer, high transparency, and high electron or hole mobility to enable efficient charge extraction. Inorganic materials like TiO_2, NiOx, and ZnO offer stability and low-cost advantages, while organic materials like Spiro-OMeTAD and fullerene derivatives improve charge transport and device performance. Interface engineering and passivation strategies are critical for minimizing recombination losses and ensuring long-term stability. As research advances, continued development of new CTL materials and interface treatments will be key to achieving higher performance and commercialization of perovskite solar cells [50].

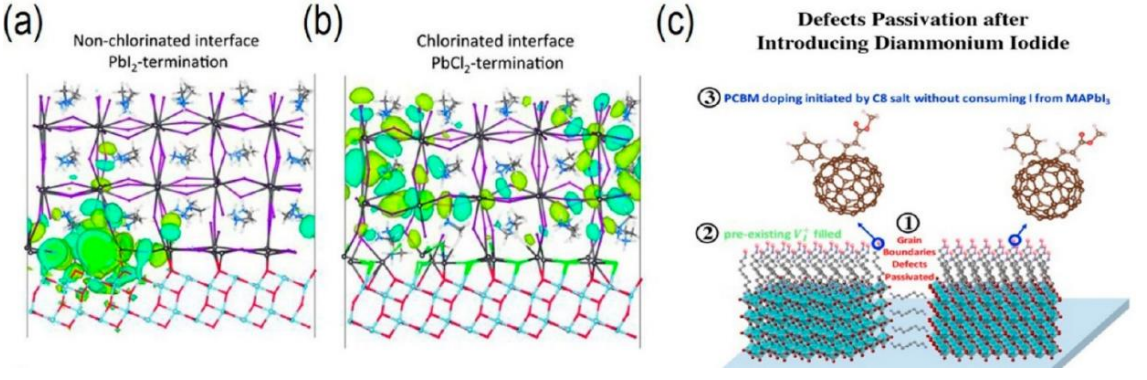

Fig. 10. a) Trap-like localized defects formed at PbI_2-terminated TiO_2/PSK interface b) Delocalized Pb-Cl defects formed at $PbCl_2$-terminated TiO_2/PSK interface c) Defect Passivation and PCBM doping effect by C8. Reproduced with permission from ref. [46]. Chen, J. and Park, N.G., 2020. Materials and methods for interface engineering toward stable and efficient perovskite solar cells. *ACS Energy Letters*, *5*(8), pp.2742-2786. Copyright © American Chemical Society.

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10. CONCLUSION

Lead-free perovskite solar cells represent a critical step forward in addressing the environmental concerns posed by conventional lead-based PSCs. This review has summarized the major advancements and challenges associated with the development of lead-free PSCs. Tin-based perovskites such as $MASnI_3$, $FASnI_3$, and $CsSnI_3$ have emerged as viable alternatives due to their direct bandgaps and eco-friendly degradation products, though challenges like oxidation of Sn^{2+} to Sn^{4+} and low PCE persist. Germanium-based perovskites, while less efficient due to wider bandgaps, demonstrate promise in alloyed forms, such as $CsSn_{0.5}Ge_{0.5}I_3$, which exhibit improved stability and moderate efficiencies. Similarly, double halide perovskites with structures like $A_2M^+M^{3+}X_6$ provide superior stability but are hindered by poor carrier mobility and transport properties. Device architecture plays a pivotal role in optimizing the performance of these materials. The p-i-n planar structure has shown better compatibility with Sn-based perovskites due to its effective charge transport and recombination suppression, outperforming the traditional n-i-p and mesoporous configurations. Additionally, advancements in charge transport layers (CTLs) and encapsulation techniques have further enhanced the stability and efficiency of lead-free PSCs. In conclusion, while lead-free PSCs currently lag behind their lead-based counterparts in terms of efficiency, they offer a sustainable and environmentally friendly alternative. Achieving competitive PCEs will require addressing the challenges of material stability, carrier transport, and crystal quality. The integration of innovative material engineering and advanced device architectures will be essential to realize the full potential of lead-free PSCs and to transition toward greener photovoltaic technologies.

11. FUTURE DIRECTIONS

The future of lead-free perovskite solar cells (PSCs) lies in overcoming their current limitations while maximizing their environmental and technological benefits. To achieve this, a multipronged approach focusing on material innovation, device engineering, and scalability is essential.

Material Development: The primary challenge for lead-free PSCs is achieving higher power conversion efficiencies (PCEs) without compromising stability. Tin-based perovskites hold great promise due to their direct bandgap and environmental friendliness; however, their oxidation to Sn^{4+} under ambient conditions remains a significant hurdle. Future research should focus on developing advanced encapsulation techniques and chemical treatments to stabilize Sn^{2+} while enhancing crystal quality and reducing defects. Similarly, germanium-based perovskites require optimization to narrow their bandgap and improve carrier mobility, potentially through alloying or introducing novel dopants. For double halide perovskites, strategies to improve carrier transport and reduce bandgap-related inefficiencies, such as incorporating novel cations or halide substitutions, must be explored.

Device Architecture Optimization: Device engineering plays a crucial role in enhancing PCE and stability. The inverted planar (p-i-n) architecture has demonstrated better compatibility with lead-free perovskites, particularly Sn-based materials. Future research should explore novel combinations of charge transport layers (CTLs) that promote efficient charge extraction and suppress non-radiative recombination. Advanced interface engineering, such as modifying the energy band alignment between CTLs and the perovskite layer, can further boost device performance. Additionally, scalable fabrication techniques like roll-to-roll printing and vapor deposition methods must be developed to enable large-scale production.

Stability Improvements: Stability remains a critical issue for lead-free PSCs, particularly in humid and oxygen-rich environments. Developing robust encapsulation materials and techniques will be key to protecting perovskite layers from degradation. Hybrid approaches combining encapsulation with material-level modifications, such as incorporating moisture-resistant additives or passivating agents, can offer synergistic stability enhancements.

Environmental and Economic Considerations: One of the primary advantages of lead-free PSCs is their environmental friendliness. Future research should focus on quantifying the lifecycle environmental impact of these materials to establish their sustainability credentials. Additionally, efforts to reduce the cost of raw materials and simplify fabrication processes will be essential for making lead-free PSCs economically viable.

Integration with Other Technologies: Integrating lead-free PSCs into tandem solar cells or hybrid photovoltaic systems can significantly enhance their overall efficiency and broaden their application scope. For example, combining perovskites with silicon or organic photovoltaics could result in tandem cells that leverage the strengths of each material. Exploring applications beyond solar energy, such as photodetectors and light-emitting diodes (LEDs), could also open new avenues for lead-free perovskites.

Theoretical and Computational Insights: Advanced computational techniques, such as density functional theory (DFT), can provide valuable insights into the electronic structure and defect properties of lead-free perovskites. These studies can guide experimental efforts by predicting the most promising material compositions and device configurations.

The path forward for lead-free PSCs involves addressing key challenges in material stability, efficiency, and scalability. By leveraging interdisciplinary approaches that combine material science, device engineering, and environmental analysis, lead-free PSCs can emerge as a sustainable and

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competitive alternative to lead-based counterparts, paving the way for a greener future in photovoltaics.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

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Availability of data and material

All of the data obtained or analyzed during this study is included in the report that was submitted.

Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Authors' contributions

All authors contributed equally in the preparation of this manuscript.

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