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A MINI-REVIEW OF RECENT STUDIES ON LEAD AND LEAD-FREE PEROVSKITE MATERIALS FOR SOLAR CELLS APPLICATION AND THEIR ISSUES

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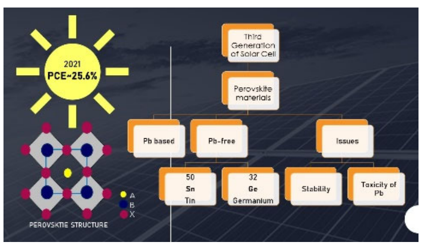
Graphical abstract



Abstract

Perovskite is gaining popularity in solar cell technologies and optoelectronics that rely on lead-based material. Perovskite solar cell (PSC) technologies are viewed as promising forthcoming innovations for their proficiency and monetary of the thin film due to high demand in the technology market. Lead-free perovskite material has become a viable alternative to lead-based perovskite, which has dominated the solar cell market for many years, due to toxicity and stability difficulties that have plagued lead-based solar cells. The large-scale commercial manufacture of lead-free halide perovskites solar cells can be expanded and its benefits in the solar field could be enhanced. Compared with lead-based perovskite, the lead-free perovskite material could also achieve a high-power conversion efficiency (PCE) indicating good solar cell performance. This review studied the perovskite materials, challenge of lead perovskite solar cell commercialization and summarizes recent research work regarding the perovskite solar cell. Moreover, this review forecast the future of perovskite solar cells in parallel with the Third Generation of Solar Cells.

Keywords: Solar cell, perovskite materials, lead-free perovskite, the toxicity of lead, stability

Abstrak

Perovskit semakin popular dalam teknologi sel suria dan optometrik yang bergantung pada bahan yang berasaskan plumbum. Teknologi sel suria perovskit (SSP) dilihat sebagai inovasi terbaik masa hadapan dari segi kecekapan dan kos saput tipis kerana permintaan tinggi dalam pasaran teknologi. Bahan perovskit bebas plumbum telah menjadi alternatif yang berdaya maju kepada bahan plumbum perovskit yang telah menguasai pasaran sel solar selama bertahun-tahun, disebabkan oleh masalah ketoksidan dan kestabilan yang melanda sel solar berasaskan plumbum ini. Pembuatan komersial berskala besar sel suria perovskite halida bebas plumbum boleh diperluaskan dan faedahnya dalam medan suria boleh dipertingkat. Berbanding dengan perovskit berasaskan plumbum, bahan perovskit bebas plumbum juga boleh mencapai kecekapan pernukaran kuasa (PCE) yang tinggi yang menunjukkan prestasi sel suria yang baik. Ulasan ini mengkaji bahan-bahan perovskit, cabaran pengkomersilan sel solar provskit berasakan plumbum dan merumuskan kerja-kerja penyelidikan terkini berkaitan sel suria perovskit. Selain itu, ulasan ini meramalkan sel suria perovskit masa depan yang selari dengan Generasi Ketiga Sel Suria.

Kata kunci: Sel Suria, bahan-bahan perovskit, perovskit bebas plumbum, ketoksidan plumbum, kestabilan

1.0 INTRODUCTION

Advances in solar cells are increasing gradually due to the high demand in energy consumption for human living. Recently, the global power demand is around 16TW and is estimated to be 30TW in 2050. This leads to the intensive and thorough study of the efficient power generation system, as the traditional technique of burning fossil fuel would not be able to supply the increased demand for electricity [1]. Hydrothermal energy, geothermal energy, wind and solar, are among the renewable energy that will help to alleviate the energy shortage. The uniqueness of solar energy can also be determined by the fact that one hour of continuous illumination of solar energy can meet our annual power needs if all the incident solar energy is converted into electricity [1]. Therefore, solar energy is a prominent energy source that leads to the global generation of electricity. Light absorber, carrier collector, and metal contact are the three elements that complete the fundamental aspects of a solar cell. A solar cell is defined as a device that directly converts light energy (photons) into electrical energy through the photovoltaic effect. This photovoltaic (PV) system has no pollution and no greenhouse gas emissions.

According to the Global Status Report on Renewables in 2020, installed renewable power capacity increased by more than 200 GW in 2019, with solar photovoltaics accounting for most of the growth. Net additions of renewable power generation capacity surpassed net installs of fossil fuel and nuclear power capacity for the fifth year in a row. However, this renewable electricity has struggled to gain a bigger percentage of global electricity output, partly due to continuous investment in fossil fuel generating capacity. PV systems are mostly rated for domestic, industrial and commercial applications for a few kilowatts to several megawatts in rooftop mounted or building incorporated systems [2].

A solar cell is categorized into generations. The first generation of solar cells presents the oldest commercially photovoltaic technology, well matured with its fabrication process. Silicon wafers were used in the first generation of solar cells and the first production of silicon solar was in 1954 with an efficiency of 6%. The simplest and most efficient solar cell on earth is the silicon solar cell due to its greatest abundance in nature, making it the best choice for photovoltaic devices. Single crystalline, multi-crystalline and amorphous silicon are the three forms of silicon used in the first generation. Nonetheless, due to the high manufacturing cost of crystalline silicon (c-Si), silicon solar cells require complex preparation and fabrication. This indicates that to make solar cells fully adopted, the initial cost must be reduced. Hence, thin film technology or solar cell emerged in the second generation.

In comparison to silicon solar cells, thin-film solar cells are always very cheap. Their efficiency is also very low, but significant research has been conducted to improve their performance over the years [2]. The materials used in thin film solar cells are Copper Indium Gallium Selenide (CIGS), cadmium telluride (CdTe), gallium arsenide (GaAs) and amorphous silicon (a-Si). Thin film cell technology consists of semiconductor material which has a direct band gap and theoretically, could produce a higher absorption coefficient and efficiency. For example, CIGS solar cell achieved more than 20% power conversion efficiency which is perfect for constructing integrated photovoltaic applications [2].

Table 1 lists the merits and demerits of wafer-based solar cells in the first generation and thin film-based for the second and third generations of the solar cell.

Thin film technologies have emerged in the third generation of the solar cell. At this stage, solar cells are currently under development and have great potential to dominate the solar market in the future [3]. Most of the materials are less commercially advanced in emerging technology and are still under investigation and research. The solar cell developed in the third generation is Organic PV, Quantum Dot Solar Cell, Dye-sensitized Solar Cell (DSSC) and Perovskite Solar Cell. In this emerging thin film technology, the goal is to produce solar cells with higher efficiency while retaining the low cost of material as well as manufacturing techniques. Among the solar cell technologies mentioned, the perovskite-based solar cell has reached a point in its technological evolutions where large-scale deployment is achievable. Scientist intends to design photovoltaic devices with high efficiency, low-cost and large-scale fabrication which are in line with third-generation solar cell but unfortunately did not succeed yet [4].

The key characteristic of a solar cell is defined by the efficiency of the device to produce electricity. Power conversion efficiency (PCE) indicates the ratio of incident photons that convert to electricity as an output. High efficiency shows a better performance of the solar cell. Figure 1 shows the PCE of silicon and perovskite solar cells in recent years.

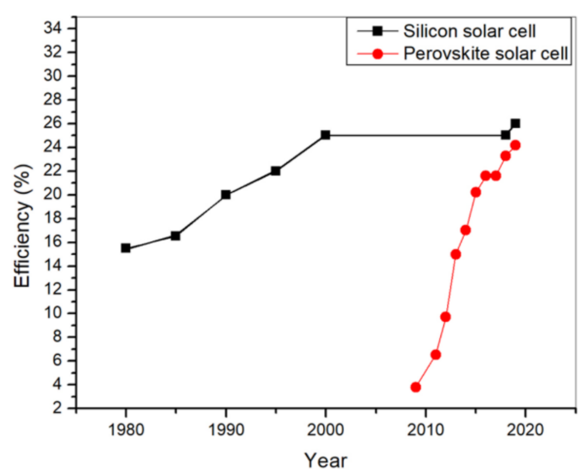


Figure 1 Power Conversion Efficiency (PCE) of silicon and perovskite solar cells from 1980 to 2020. Adapted from Ref [1]

Table 1 The merits and demerits of solar cells. Adapted from Ref [2]

Solar cell type	Merits	Demerits
Wafer-based	• Tested technology • Easy fabrication process • Reliable • Inexpensive • Plentiful and non-toxic • High power conversion energy	• Low absorption coefficient • Demand often exceeds • Efficiency decreases as temperature increases
Thin film based	• Easy production for high volume • Highly efficient when the temperature is very high • Flexible and lightweight	• Low power conversion efficiency • Toxic materials are used • Low stability • Short lifetime

2.0 PEROVSKITE SOLAR CELL

Perovskite materials catch the attention of most researchers because of their abundance in nature, strong solar absorption, low non-radiative carrier recombination and non-toxic material of solar cells [2, 5-8]. It has led to the development of scientific studies, especially in telecommunication and microelectronics fields such as superconductivity, magnetoresistance, ionic conductivity and gathering of dielectric properties [2].

The most significant parts of perovskite solar cell fabrication for successful commercialization are simplicity, low manufacturing cost, higher PCE and easiness of production [9-13]. Generally, perovskite is a material that forms a crystal structure with a cubic unit cell. Perovskite is made up of Group IV elements such as silicon (Si), lead (Pb), tin (Sn) and germanium (Ge). The perovskite is composed of $CaTiO_3$ mineral in the name of Russian mineralogist Count Lev. A. Perovskite. It has a general chemical formula of ABX_3 and the structure is stabilized by electrostatic interaction between A and B-X (Figure 2). A and B are referred to as organic and inorganic cations while X is a halogen anion. For cation A to form a close-packed perovskite structure, its size should be small enough to fit into four adjacent MX_6 octahedra.

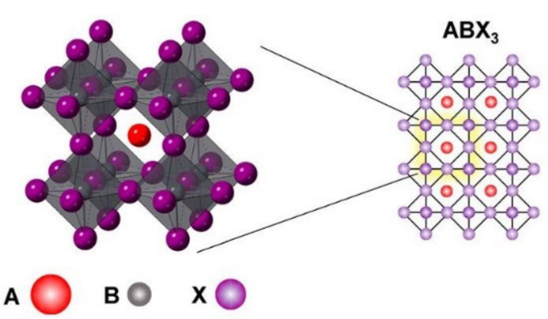


Figure 2 Crystal structure of 3D perovskite. Adapted from Ref [14]

Perovskite is also known as organometal halide which has a good charge carrier mobility and diffusion length [15]. It is a semiconductor material that absorbs photons when light passes through it and allows the transportation of the charge carrier to conduct electricity. It has good photoelectric properties, lower excitation binding energy, high optical absorption, longer diffusion length, great PCE and longer lifetime of the carrier [16, 17]. The best options for developing efficient and cost-effective solar cells are organic-inorganic hybrid-perovskite (OHIP) materials due to their advantages in exhibiting unique optical and electrical properties [18]. Typically, a perovskite solar cell is a structure consisting of a perovskite absorbent layer placed between the hole transport layer (HTL) and the electron transport layer (ETL) as shown in Figure 3. As the solar cell is exposed to sunlight, there will be the separation of the charge carrier (electrons and holes) into p-type and n-type regions followed by the extraction of the charge carrier to generate electricity.

Generally, perovskite solar cells are new third-generation solar cells that contribute to the large scale of solar cell production in terms of their PCEs and compatibility with a scalable process. Perovskite solar cell (PSC) is a type of solar cell that includes a structured c compound of perovskite material which works as an active layer in the solar cell. It could absorb photons and uses less than 1 µm of material to capture the same quality amount of sunlight. A perovskite can be grouped into two categories based on the type of oxide: inorganic oxide and halide perovskite.

A solar cell device is a p-n junction diode made of p-type and n-type semiconductors. When the light hits the solar cell, some of the photons of the light rays are absorbed and release electrons. The light energy supplies efficient energy to the junction and creates electron-hole pairs. The free electrons in the depletion region move to the n-type side of the junction while holes in the depletion move to the p-type side of the junction. When the concentration of electrons and holes becomes higher in n-type and p-type, the p-n junction will act like a battery cell. As a completed circuit is connected to the electrodes, the free electrons will travel through the circuit creating a flow of electricity and voltage called photovoltage.

In conclusion, a solar cell is a form of photovoltaic cell that has electrical characteristics such as current, voltage or resistance. Solar panels can be formed by combining individual solar cells.

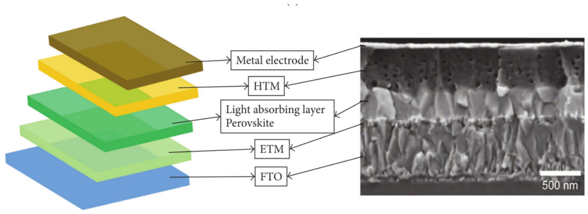


Figure 3 Structure of perovskite solar cell (PSC). Adapted from Ref [16]

3.0 PEROVSKITE-BASED MATERIALS

3.1 Lead (Pb)

Lead (Pb) is also proven as the best material for absorbing layers in the solar cell by its excellent visible absorption, adjustable bandgap, and high carrier diffusion length. Pb is found in nature as Pb in minerals and is ubiquitous in the environment [19]. Over the years, Pb-based perovskite absorbing layers have presented a huge contribution to solar cell technologies. An excellent capacity for energy conversion into electricity is one of the upsides of Pb material. Due to its straightforward synthesis technique and ease of device fabrication in regular and inverted form, methyl ammonium lead iodide ($CH_3NH_3PbI_3$ or MAPI) has been the most common and thoroughly investigated perovskite material among the different perovskite materials. Recently in 2021, the highest PCE recorded for perovskite solar cells reached 25.6% (certified 25.2%) making it the world's best record [20].

From Figure 4, the target PSC had a maximum PCE with short-circuit current density (J_{SC}) of 26.35 mA cm^{-2} and the open-circuit voltage (V_{OC}) of 1.89 V and fill factor (FF) of 81%. This best record was investigated using formamidinium lead iodide ($FAPbI_3$), which is known for its thermal stability and narrow bandgap. By introducing the pseudo-halide formate ($HCOO^-$) to the precursor materials, the scientists increased the efficiency of the cell by limiting the number of defects in the perovskite structure and having long-term operational stability for about 450 hours.

A previous report revealed that pre-heated treatment onto Pb-based PSC deposited using a two-step deposition spin coating technique could produce almost 8.4% of PCE [21]. Technically, the photovoltaic performance for the solar cell is depending on the short-circuit photocurrent density, the open-circuit photovoltage, the fill factor of the cell and the intensity of the incident light [21]. At this point, a smooth, crystallinity-rich, and pinhole-free surface explains the efficiency enhancement of the solar cell. The researchers found that the pre-heating of PbI_2 films before spin coating can be used to modify the perovskite layer and enhance the performance of perovskite solar cells, which explains how pre-heating the material during fabrication can enhance the performance of the solar cell. In another study, Pb-based perovskite material achieved a good PCE of close to 10.38% with higher surface coverage, uniform and better crystal quality [22]. The researchers investigated and claimed that the concentration of 1.0 M of PbI_2 and 0.063 M of MAI were the best for producing the highest efficiency.

Figure 5 indicates the PSC structure prepared using the most straightforward deposition technique which is spin coating with different precursor concentrations. Due to its easy advantage of producing high efficiency and good performance, Pb-based solar cells continue to pique the interest of many researchers these days.

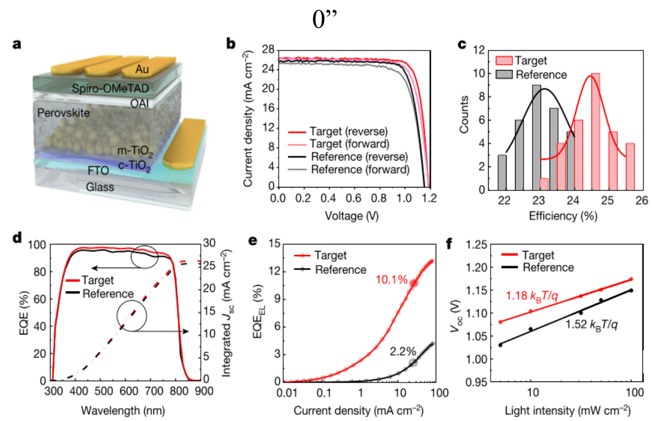


Figure 4 Characterization of the photovoltaic performance of the $FAPbI_3$ PSC. (a) The configuration of $FAPbI_3$ PSC devise, (b) J-V curve of the reference and target PSCs under both reverse and forward voltage scan, (c) The distribution of the PCEs of the reference and target of PSCs, (d) EQE and integrated J_{SC} of the reference and target PSCs, (e) EQE_{EL} measurement under current densities from 0.01 mA cm^{-2} to 100 mA cm^{-2}, and (f) The relationship between measured V_{OC} and the light intensity for the reference and target PSCs. Adapted from Ref [20]

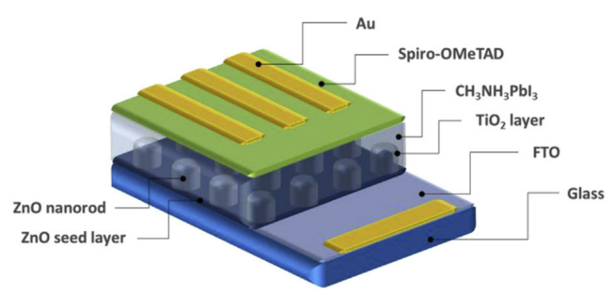


Figure 5 Schematic depiction of the perovskite solar cell based on ZnO-TiO_2 nanorod array. Adapted from Ref [22]

Despite the success of Pb-based perovskite, the researchers claimed that the main concern with materials is the toxic nature of Pb, poor stability and the scientific challenge to replace it with less toxic materials [5, 23-25]. Toxicity of Pb becomes a challenge in commercializing this perovskite absorbing layer which restricts it from the various specialized application. The chronic poisoning of Pb is well understood and documented. For example, Pb can be harmful to humans when this material leak from the solar panel due to insolubility. Even though Pb-based perovskite demonstrates a significant attraction in solar cell technology, it could produce toxicological concerns that could affect both human beings and the environment. Therefore, due to the perilous and lack of adaptability to human life, further research on perovskite material remains debated. It creates a noticeable gap in this research area. In light of this, the quest for alternative perovskites has recently been a prominent focus of research.

3.2 Tin (Sn)

Due to its presence in the same group as Pb in the Periodic Table, tin (Sn)-based perovskite can replace Pb because its properties are comparable to one another based on its satisfactory performance. By considering the Gold-Schmidt tolerance factor, Sn-based inorganic perovskites must have a highly stable geometrical structure than Pb [26].

In addition, Sn-based perovskite proposed good film properties, thus its characterization should be comparable to Si and Pb material. To support this statement, Sn is a non-toxic material that has good charge-carrier mobility and a small band gap (1.3 eV) which displays an excellent optoelectronic property. Indeed, Sn-based perovskites are also known as lead-free materials that possess good morphologies of thin films, including smooth surfaces, tightly packed grains, good surface coverage, and preferred crystal orientations [7]. Therefore, Sn-based solar cells are a feasible alternative for future solar cells due to their low toxicity[23], show good semiconducting properties [5] and have become essential in optometry [27].

Generally, the Sn-based perovskite layer of solar cells has become a peak of interest among researchers. The utilization of Pb-free material is fundamentally a renewal of Pb material as an absorbing layer in the solar cell. Less toxicity of the material is the biggest reason for enhancing the Pb-free perovskite material in solar cell applications. Figure 6 shows the comparison of efficiencies between Pb-based perovskite and Pb-free perovskite solar cell. The data clearly shows that Pb-free materials such as tin, offer significant advantages and the ability to produce high PCEs that are comparable to Pb-based PSC.

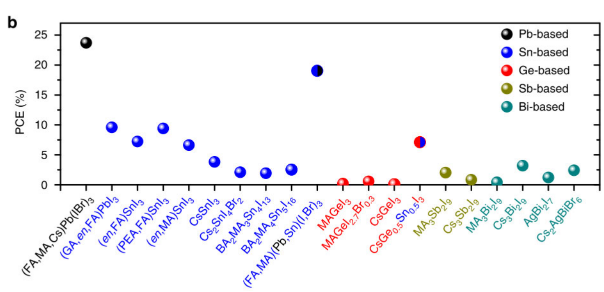


Figure 6 Efficiencies report of representative solar cells for lead-based and lead-free perovskite. Adapted from Ref [23]

Previously, a tin-based perovskite solar cell was developed using methyl ammonium tin iodide ($MASnI_3$) via ion exchange. 7.78% of PCE with high stability was successfully recorded and was the highest value for $MASnI_3$-based material [28]. The researchers declared the solid-gas reaction approach between SnF_2 and gaseous MAI (as precursor solution) could produce highly uniform and pinhole-free perovskite film. This is due to the fact that SnF_2 with a high percentage can effectively prevent Sn oxidation. The improved PCEs are due to the improvement by J_{sc} values and FF which are 20.68 mA cm^{-2} and 0.66 respectively. To conclude, tin is the best alternative to replace Pb-based perovskite due to its non-toxic nature and the ability to produce a high-performance PSC.

Among other alternatives to replace lead in solar cell applications, tin-based perovskite produced a high PCE of over 13%. Nishimura *et al*. reported the research of fabricating tin halide perovskite solar cells by regulating the A site cation to achieve a tolerance factor of 1[29]. It has been shown that partial substitution of ethylammonium cation (EA cation) for formamidinium cation gives a more stable perovskite as shown in Figure 7. The researchers claimed that incorporating the EA cation into the GeI_2 doped ($FA_{0.98}EDA_{0.01}SnI_3$) aligns the perovskite energy level to match the charge transport layer, therefore increasing the intrinsic potential. The highest PCE of the solar cell was determined by EA0.1 which is 13.24% (Table 2). It is the highest PCE reported for tin halide perovskite at present. This indicates that EA substitutions enhanced tin perovskites' energy levels, allowing charge to be extracted into the charge transport layers and thereby reducing the recombination of charge carriers. This idea tells that tin halide perovskite has good potential to compete with toxic lead material and become the most efficient and stable perovskite in PSC. Based on previous research, the researchers stated that the J_{SC} of tin-based solar cell is still considered as high value, but its V_{OC} is still low, resulting in low PCE of a tin-based solar cell. High loss in V_{OC} is because of severe recombination and unmatched band alignment in the device [30].

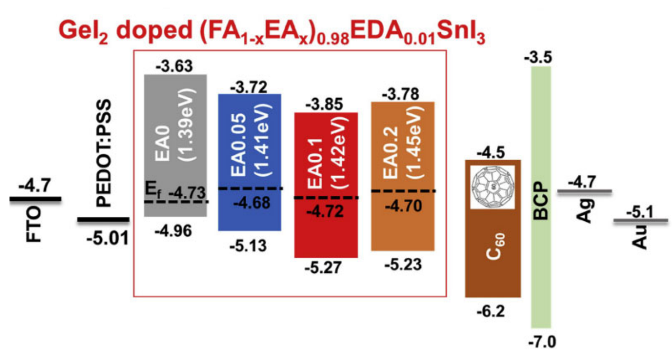


Figure 7 Efficiencies Schematic diagram of energy band levels for the inverted tin halide PSCs. Adapted from Ref [29]

Table 2 Photovoltaic parameters of best EA0, EA0.1 and EA0.1-EDA passivation of perovskite solar cell. Adapted from Ref [29]

SAMPLE		J_{sc}(mA cm^{-2})	V_{OC}	FF	PCE (%)
EA0	FORWARD	23.15	0.54	0.72	9.03
	REVERSE	23.23	0.56	0.64	8.28
EA0.1	FORWARD	22.04	0.70	0.73	11.35
EA0.1	FORWARD	23.83	0.65	0.76	11.75
	REVERSE	23.78	0.66	0.72	11.20
EA0.1(EDA passivation)	FORWARD	20.32	0.84	0.78	**13.24**
	REVERSE	20.38	0.84	0.74	12.64

3.3 Germanium (Ge)

Germanium (Ge) which exists in a group of 14 elements similar to Pb, is another promising contender for perovskite solar cells. Ge contains fewer toxins and is more plentiful on Earth. Ge-based perovskite solar cell Is another Pb-free perovskite solar cell with strong characteristics comparable to Pb-based perovskite solar cell because Ge shows similar optical properties as Pb. Due to their well-suited optical characteristics for solar applications, Ge halide perovskites are an intriguing alternative to Pb-based perovskite. Recently, Yang *et al.* developed the high luminescent Ge-Pb perovskite films with efficiencies up to 71% and showed ~34% of considerable relative improvement over similarly prepared Ge-free, Pb-based perovskite films. Figure 8 shows the optical properties and morphology of Ge-Pb perovskites with an optical bandgap around 2.4 eV.

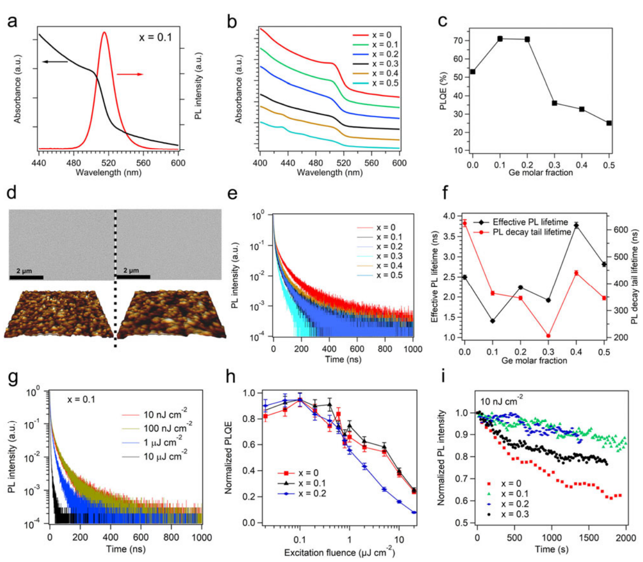


Figure 8 Optical properties and surface morphology of the Ge-Pb perovskite samples. Adapted from Ref [31]

Current research shows that Ge -based perovskite is inferior to Sn-based. Therefore, it has been challenging to make stable and high-performance solar cells with Ge-based perovskite material [23]. Otherwise, a report by Chen *et al*. demonstrated the all-inorganic cesium tin-germanium triiodide ($CsSn_{0.5}Ge_{0.5}I_3$) solid-solution perovskite with efficiency up to 7.11%. They claimed that this light absorber material shows high stability, with less than 10% decay in efficiency even after 500 hours of continuous operation under an N_2 atmosphere [25]. This is because the photovoltaic performance of perovskite was improved by injecting native oxide passivation onto the perovskite surface when exposed to air. Figure 9 describes the Sn-Ge perovskite which is sandwiched between ETL and HTL layer with a thin native oxide layer between perovskite thin film and HTL. The researchers also declared that PSCs' remarkable performance is due to the formation of a full-coverage, stable native-oxide layer that completely encapsulates and passivates the surface of the perovskite layers. In conclusion, the native-oxide passivation method described here is another way to improve the efficiency and stability of Pb-free PSCs.

Previous research also claimed that Ge^{2+} tends to be more stable than Sn^{2+} in terms of oxidation issues, making Ge a more suitable material for improved stability of perovskite solar cells [32]. Another research reported that methylammonium tin iodide, MAGeI3 has a remarkable hole and electron transport conductive behaviour and adequate stability compared with $MAPbI_3$, hence, suggesting that this germanium-based perovskite may be competitive and environmentally friendly to Pb-based PSC [33].

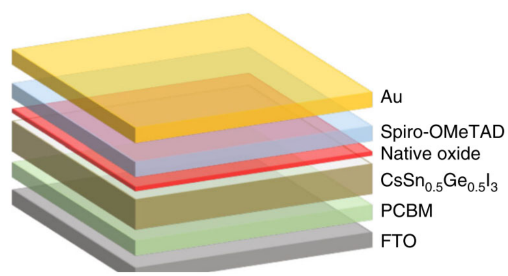


Figure 9 Schematic illustration of PSC device structure. Adapted from Ref [25]

4.0 MAIN ISSUES IN PEROVSKITE SOLAR CELL

4.1 Stability of PSC

To the best of our knowledge, the heart of the solar cell is the absorbent layer responsible for absorbing as many photons as possible. Thus, the best performance of perovskite solar cells should be developed. The rapid advancement in performance suggests that PSCs have great potential, surpassing the traditional silicon solar cell. Unfortunately, perovskite materials show unstable properties [34].

The instability of perovskite solar cells is determined by several factors such as air, light stability, thermal stability, counter electrode, encapsulation, surface defect and moisture (Figure 10). For example, perovskite solar cells are influenced by moisture and oxygen factors because the devices are prone to degradation where the presence of H_2O and O_2 affects chemical stability [34, 35]. The long diffusion length and best carrier charge mobility of single crystals perovskite make them more stable. However, Huang *et al.* proposed that single crystals exhibit poor stability since their O atomic percentage is only 45.65% [27]. This is due to the formation of a large amount of Sn vacancies that will oxidize the Sn halide perovskites. As a result, it is essential to avoid air and water contact during perovskite preparation. To deal with this issue, the researchers are focusing on several types of protective materials to encapsulate the perovskite, protecting it from air and moisture.

On the other hand, the direct exposure of PSC to sunlight causes degradation in thermal stability. As a result, the solar panel's temperature will rise to or more than 85 ℃. At this stage, the PSC device may not be widely used in actual daytime because the internal heat accumulation is decreasing [34]. Therefore, it is crucial to understand that temperature can affect the performance of the photovoltaic device.

Li *et al*. proposed the ionic liquid n-butylammonium acetate (BAAc) to address oxidation issues resulting from disordered crystal growth and low defect formation energy. This is related to Sn^{2+} oxidation to Sn^{4+}. The coordination of BAAc with Sn allows for the control of perovskite crystallization in thin films. BAAc-containing perovskite films produced as a result are more compact and have a preferred crystal orientation. The results show that BAAc lowers carrier combination, and inhibits oxidation of Sn^{2+} and increases the stability of the perovskite crystal structure. Thus, 10.4% of the PCE was successfully achieved by maintaining 96% of its original efficiency for 1000 h after storage in the dark with nitrogen ambient [36].

Perovskite is regarded as the solar cell of the future. Despite the tremendous progress of solar cells, the stability of perovskite solar cells remains a significant challenge in maintaining their performance. To date, comparable silicon solar cell efficiencies have been successfully achieved but improved device stability still needs to be ensured [1]. It is challenging to maintain stability while simultaneously achieving higher efficiency. Poor stability and faster degradation of device performance of perovskite materials are the most prominent problems, and this is a major obstacle to achieving comparable performance to lead-based perovskite [37]. As a result, understanding degradation mechanisms and related factors are critical for improving device stability and performance.

Overall, the poor stability of perovskite will limit its application mainly in solar cell technology. Therefore, the solar cell's stability must consider the whole system of the device including layers and interfaces within the solar cell device. Suitable encapsulation and improved inherent stability of perovskite film to moisture, are the two main approaches that must be considered to enhance the stability of solar cell devices [38]. The studies of solar cell stability are shown in Figure 11.

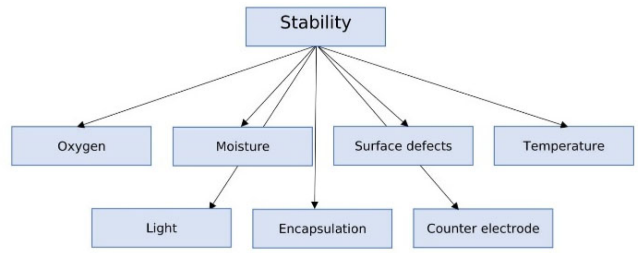


Figure 10 Perovskite stability factors [35]

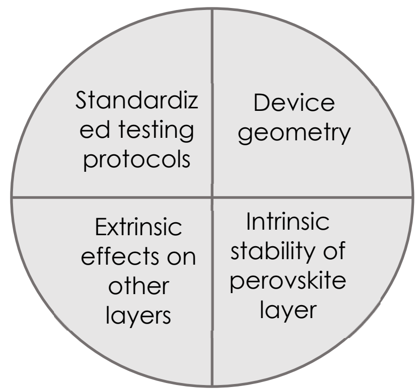


Figure 11 Key issues of future research on perovskite stability. Adapted from Ref [38]

The stability of PSC can be improved by two elements: intrinsic material and the device itself towards environmental factors. Based on the latest research and understanding of the degradation of PSC, the stability of solar cell devices has been improved in terms of morphology degradation, ion migration, surface and bulk chemical reaction, and crystal structure transition [39-43]. However, to further improve the stability of PSCs under their operating conditions, external encapsulation is necessary [39, 44-49]. The purpose of PSC encapsulation is to prevent the intrusion of moisture and oxygen, therefore the selection of appropriate encapsulation is very important, but this approach is falling far behind the research progress [39].

Akman *et al.* (2020) proposed that the stability of PSC can be improved by introducing a passivation agent known as 2,3,4,5,6-pentafluorobenzyl phosphonic acid (PFBPA) molecule onto α-$FAPbI_3$ perovskite. By using PFBPA passivation, the efficiency of perovskites was improved above 22% and even more stable on a long-term basis. The moisture stability of perovskite is proven and maintains >90% initial efficiency after 600 hours [50]. PFBPA passivation layer helps to overcome the grain boundary defects on the surface of $FAPbI_3$ perovskite, reduce the charge recombination, protect the perovskite structure from moisture problems and achieve long-term stability in the ambient environment.

The introduction of bulky organic cations with suitable coadditive for PCS is another way to improve device stability [51]. The stability of tin-based perovskite can be improved by replacing an organic cation of methylammonium (MA^+) with formamidinium (FA^+). The interaction of organic cations (FA^+) with the inorganic framework was stronger in $FASnI_3$ than in $MASnI_3$. Therefore, the PCE of FA^+ cation is 5.5%, higher than MA^+ [52]. As of now, $MASnI_3$ and $FASnI_3$ PSC have recorded the highest PCE of 7.78% and 13.83% [52, 53]. In conclusion, organic cations play an important role in the performance and stability of PSC, especially for tin-based materials. The issues must be resolved for perovskite solar cells to have a long operating life compared to traditional solar cells.

4.2 Toxicity of Lead-based PSC

The major issue with solar panel generation is its relatively low performance and high fabrication cost for large-area photovoltaics. Previously, silicon and lead-based perovskites which are major contributors to solar cell technology are not economical relative to grid-based energy supplies. The high cost of silicon-based raw materials and the toxicity issue of lead-based turn into an obstacle to bringing these products into the market.

For Pb-based PSC, it raises toxicological concerns that could negatively affect human health and the environment. This is owing to the insolubility of Pb-based materials, which could cause leakage from the solar panel. The research conducted by Schileo *et al.* stated that it is well known and documented the effects of acute and chronic Pb poisoning where Pb compounds enter the bloodstream through ingestion, inhalation, or dermal contact. Besides, chronic Pb poisoning causes neurological disorders in terms of decreased intelligence, deficits in motor function and behavioural problems (anxiety, depression and violence) [19]. In addition, Schileo *et al.* mentioned that the effect of non-neurological include decreased fertility, cataracts, hypertension, and cardiovascular and renal diseases. The hazardous exposures of Pb and their consequences are shown in Table 3.

Therefore, due to lead's dangerous nature and its inability to adapt to human life, various further studies relating to perovskites are still debated. This toxicity issue of Pb also prevents the large-scale production and photovoltaic field application of Pb perovskite [54]. Although Pb-based perovskite dominates solar cell technology, its environmental impact must be considered. Hence the best alternative would be the replacement of Pb with elements of the same group in the periodic table [55]. After several years of research, researchers have already gained some understanding of the lead-free perovskite system and the core of lead-free perovskite research focuses on the elimination of Pb in PSCs [54].

An ideal candidate for Pb-free should have low toxicity, narrow direct bandgaps, high optical absorption coefficient, high mobility, good stability and so on [23]. The potential materials for PSC must have a direct bandgap of around 1.1 to 2.0 eV, as shown in Figure 12.

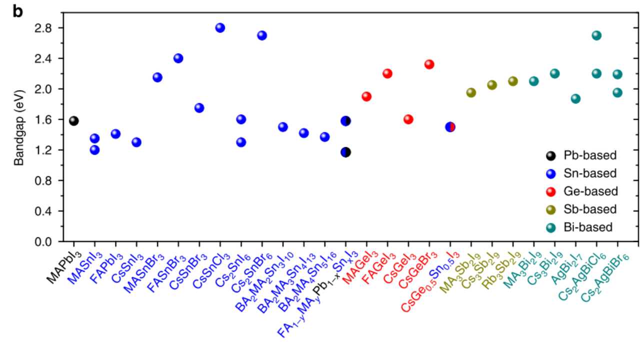


Figure 12 Bandgaps of various materials. Adapted from Ref [23]

Table 3 Hazardous of Pb and their consequences. Adapted from Ref [2]

Toxicity of Pb dosage	Consequences
100-150 µg/dL exposure for less than 14 days	Kidney and brain damage to adults
15-30 µg/dL exposure for less than 14 days	For middle-aged people, blood pressure is increased
10-15 µg/dL exposure for less than 14 days	Mental ability and birth weight is reduced in infants for pregnant women
15-20 µg/dL exposure for more than 14 days	The growth rate is reduced for the children

5.0 CONCLUSION AND FUTURE PERSPECTIVE

The research regarding this perovskite absorbing layer can be further developed by improving the stability and performance of the solar cell. Just like traditional solar cells in the first and second generations, perovskite material has become a great focus of researchers and scientists as it brings innovation and impacts the development of solar cell technologies in the world.

Various fabrication processes and novel perovskite compounds have been developed to construct high-performance solar cells. Even though there is a lot of research going on in the field of perovskite solar cells, there are still a lot of obstacles to overcome. Scientists or researchers are diligently working to develop the next generation of perovskite solar cells that will be more stable and have higher PCE.

The properties or characteristics of perovskite solar cells are influenced by many factors, including controlled parameters such as precursor concentration, annealing temperature, fabrication technique, types of material, as well as uncontrolled aspects such as nature of the material (toxicity), environmental changes and even the stability of PSC itself. Stability, efficiency and production costs are the integral parts of solar cells [35].

Therefore, this review outlines current research on perovskite for Pb and Pb-free materials and the issue of stability and toxicity among perovskite solar cells that contribute to the deterioration of solar cell generation. The performance of PSC is based initially on the perovskite material itself and the lifetime of solar cell devices. Overall, Sn-based perovskites are mentioned to be the best replacement for Pb-based, however, its stability is still far from the understanding. Theoretically, the stability of Sn is said to be less than Pb.

Despite this, the non-toxic nature of Sn makes it the best solution to the toxicity problem, although its PCE has not yet reached more than 15%. Another contender for Pb-based perovskite, Ge, is also being investigated as a means of obtaining high PCE. The mixture of Ge and Sn as perovskite solar cells currently showed 'positive feedback' to device performance. Table 4 shows the most recent studies on perovskite solar cells with their PCE. From the table, we can see that Pb-based perovskite still produces high PCE despite having toxic properties compared to other materials. Over recent years, the PCE value of PSCs depends on the perovskite-based material and the fabrication method. Various methods are used by researchers to prepare and fabricate the solar cells such as spin coating, modified solvent bathing, slot die printing and so on. The spin coating method is the most preferred method by researchers because of its simple technique compared to other techniques. Tin-based solar cells have also achieved a PCE value of 25.76%, which is the highest value ever recorded in solar cells, allowing them to surpass the highest PCE value recorded by Pb-based PSCs of 25.6% in 2022.

Therefore, researchers may argue that using lead as a PSC needs to be maintained to generate electricity at higher levels. From another angle, the study of Pb-free materials is also developing in parallel with that of lead perovskite materials. Various factors, fabrication techniques and parameters are analyzed and optimized in various studies to find high PCE solar cells so that they can replace lead-based solar cells.

Table 4 Recent work on Perovskite Solar Cell

Perovskite	Technique of Fabrication	Open circuit voltage, V_{OC} (V)	Band gap (eV)	Efficiency (%)	Year	Ref.
$CH_3NH_3SnI_3$	Spin coating	0.88	1.23	6.00	2014	[5]
$CH_3NH_3PbI_3$	Fast deposition-crystallization	0.98	-	13.90	2014	[9]
$CH_3NH_3PbI_3$	Spin coating	0.938	-	11.66	2014	[56]
$CH_3NH_3PbI_3$	Spin coating	0.84	-	11.12	2015	[57]
$MASnI_{0.5}Br_{2.5}$	One-step deposition	0.80	-	1.51	2016	[58]
$CH_3NH_3SnI_3$	Hybrid thermal evaporation	0.494	-	1.70	2016	[7]
$CH_3NH_3SnI_3$	Modified solvent bathing	0.45	-	2.14	2017	[59]
$CH_3NH_3PbI_3$	Spin coating	0.72	-	9.77	2017	[60]
$CH_3NH_3PbI_3$	Spin coating	1.18	-	16.21	2017	[61]
$CH_3NH_3PbI_3$	Slot die printing	0.82	-	9.40	2017	[62]
$CH_3NH_3PbI_3$	Spray pyrolysis	1.041	-	17.40	2017	[63]
$CH_3NH_3PbI_3$	Two-step process	0.97	-	17.42	2018	[64]
$CH_3NH_3PbI_3$	Two-step sequential deposition	0.92	-	10.38	2018	[22]
$CH_3NH_3SnI_3$	Two-step process	0.486	-	7.13	2019	[65]
$CH_3NH_3PbI_3$	Pre-heated treatment/spin coating	0.87	-	8.42	2019	[21]
Carbon films for PSC	Spin coating	0.90	-	13.30	2019	[66]
$CsSn_{0.5}Ge_{0.5}I_3$	Vapor-processing	0.63	-	7.11	2019	[25]
$CsPbBr_3$	Multistep spin coating	1.310	-	8.79	2019	[67]
$CH_3NH_3SnI_3$	Ion exchange/insertion reaction	0.570	-	7.78	2020	[28]
$CH_3NH_3Sn_{(1-x)}Ge_xI_3$ ($0 \leq x \leq 0.5$)	First-principal calculation	-	1.38 - 1.61	25.76	2020	[68]

Perovskite	Technique of Fabrication	Open circuit voltage, V_{OC} (V)	Band gap (eV)	Efficiency (%)	Year	Ref.
$FASnI_3$ (BAAc-containing perovskite)	Spin coating	0.650	-	10.40	2021	[36]
Cs_2TiBr_6	Capacitance simulator	1.530	-	11.49	2021	[69]
Cs_2TiBr_6	Simulation SCAPS-ID software	-	1.60	17.83	2021	[70]
$FAPbI_3$	Spin coating	1.112	-	22.25	2021	[50]
$FAPbI_3$	Spin coating	1.189	-	25.60	2021	[20]
$FASnI_3$	Spin coating	0.850	1.41 - 1.42	13.82	2022	[53]

To conclude, further research should be conducted in the future to increase the device's stability and performance of solar cells. Although this study has been realized over the past few years, a solution is still being sought. We can conclude that researchers continue to choose perovskite for research on improving solar cell technology as a source of energy for humans. Until now, they have been putting in a lot of effort to strive for the highest PCE of solar cells by considering a variety of factors such as the cost of manufacture, the type of perovskite material used, and, most crucially, the safety for humans and environment. Therefore, the discovery of Pb and Pb-free perovskite material should be able to produce excellent efficiency, low cost and easy production. So that it is compatible with the 3rd Generation of Solar Cell.

To achieve this, all aspects that affected the performance of perovskite solar cells should be considered. As perovskite technology matures into a commercial concept, various challenges become more prominent for researchers. Solar cell technology with an average lifespan of over 25 years will be the focus. Therefore, it is elucidated that more promising outcomes will emerge in this field of research.

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