

# Prospects for Tin as a Non-Toxic Replacement for Lead Perovskite Solar Cells

Adaline Farrow || 260966721

McGill University Department of Chemistry

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## Abstract

As crystalline silicon solar cells reach their hypothetical Power Conversion Efficiency (PCE) limits, Lead Halide Perovskite Solar Cells (LHPSCs) offer an improvement to efficiency, but come at the cost of environmental toxicity. Tin's isovalence makes it a suitable non-toxic replacement, the Perovskite Solar Cells (PSCs) of which currently report PCEs of approximately 14%, roughly half of what has been achieved using LHPSCs. This review constitutes a brief summary of the Shockley-Queisser limit, as well as a highlight on current tin PSC technologies. Notable achievements in PCE and device lifetime are summarized. Finally, improvements in both technologies as well as tandem cells are contrasted to determine the prospects of solar energy technology.

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# 1 Introduction

As global energy demands increase, reserves of fossil fuels are being used up faster leading to further concerns surrounding climate change. A shift towards greener energies is becoming imperative. Of the available green energy sources, solar energy is a functionally limitless resource hindered only by our ability to capture it. With the most efficient solar energy absorption band gaps being anywhere between 1.0 and 1.8 eV<sup>[1]</sup>, sunlight gives us a broad range of band gaps to shoot for when engineering solar cells. Ideally, one would be able to harvest all the energy coming from the sun, but that is easier said than done. Crystal silicon (c-Si) solar cells sit comfortably within this range at 1.1 eV<sup>[2]</sup>. They are easy to synthesize, have low degrees of impurity, and are relatively quite stable at long time intervals. However, the improvement in power conversion efficiency (PCE) of c-Si cells is not matching our rapidly increasing energy demands, as the PCE of modern c-Si solar cells is beginning to reach its theoretical limit. The current highest recorded PCE for c-Si cells is 26.8%<sup>[3]</sup>. Theory states that these cells will reach their limit at a PCE of approximately 29.4%<sup>[3]</sup>. This stagnation in PCE advancement has prompted a shift to a different family of materials with even higher potential PCEs and more desirable optoelectronic properties.

The family of materials in question is that of perovskites. Perovskites generally adhere to the chemical formula  $ABX_3$  (or variations thereupon) wherein A is a metal or organic cation, B is a metal ion, and X a chalcogen or halogen. These materials have been discovered to have superior photonic properties that are being studied in the fields of photovoltaics, optoelectronics, and photocatalysis<sup>[4]</sup>. As a result these materials are becoming one of the

most interesting and applicable materials in current research. The ability to engineer a large array of optical and electronic bandgaps with high tunability, as well as their relatively facile synthesis make them highly desirable materials. Metal halide perovskites (MHPs) typically follow the generic  $ABX_3$  format with the most popular being formamidinium lead triiodide (FAPbI<sub>3</sub>) and methylammonium lead triiodide (MAPbI<sub>3</sub>). These materials form a large array of crystal structures depending on composition (Fig. 1)<sup>[5]</sup>, allowing for ease of bandgap and physical property engineering. This tunability, along with their facile synthesis makes them prime candidates for the future of solar cell technology.

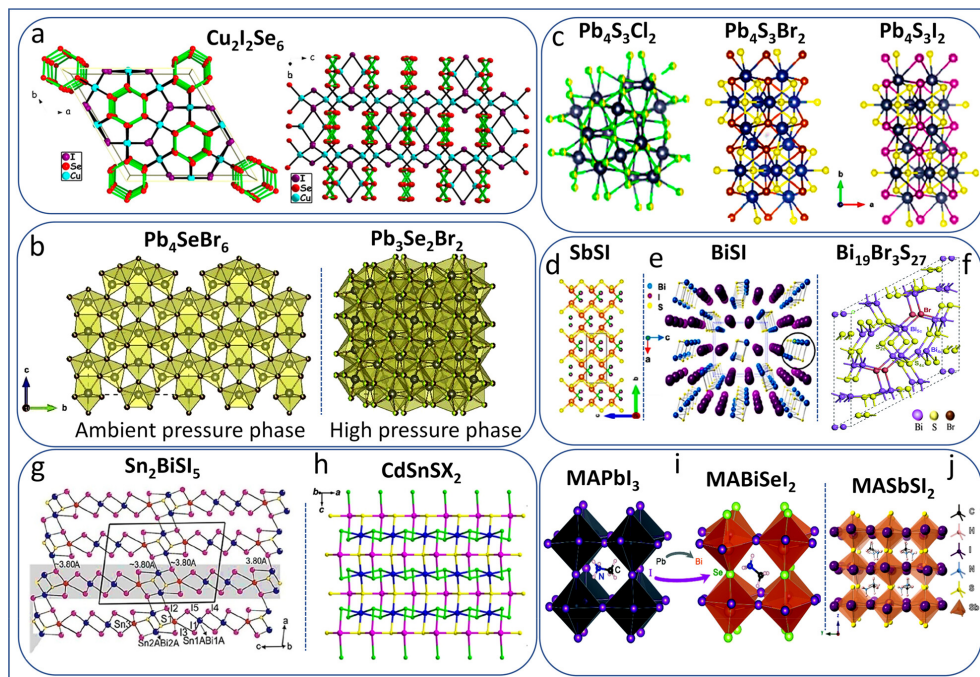


Figure 1: Crystal Structures of Different Perovskites. Adapted from (Shyamal, 2023).

Perovskite solar cells (PSCs) are garnering large amounts of attention from the scientific community as of late, due to the c-Si solar cells reaching their theoretical limits. Single junction PSCs have been measured to have PCEs of up to nearly 30% despite starting at

roughly 3.8% only 13 years ago<sup>[6]</sup> (Fig. 2)<sup>[7]</sup>. This, as compared to c-Si, has been an explosion in efficiency. Furthermore, perovskite/c-Si tandem cells have been theorized to have PCE limits above 40%<sup>[3]</sup>. The biggest drawback with metal halide perovskites (MHPs) is that they typically contain highly toxic lead. The toxicity of this heavy metal and concerns surrounding environmental leakage are making it difficult to mass produce and commercialize lead halide perovskite solar cells (LHPSCs)<sup>[8]</sup>. These issues are driving many to research greener alternatives such as heavy metal free perovskites. Isovalent metals such as Sn 2+ are becoming promising alternatives that could replace the Pb 2+ that is used in most MHPs.

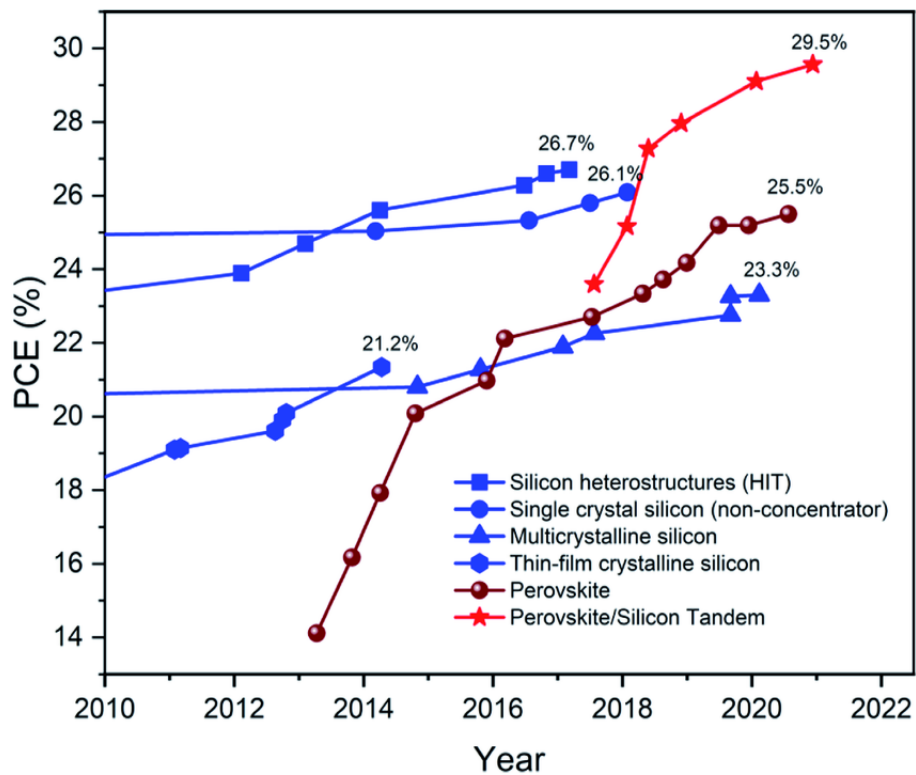


Figure 2: Efficiency of Various Solar Cell Technologies Over Time. Adapted from (Shrivastav, 2021).

The advent of tin (Sn) based PSCs is rather recent with the earliest attempts being made in the mid-2010s. These early attempts resulted in very low PCEs of around 5%<sup>[8,9,10]</sup>. However since then, these materials have risen to a high of 14.6% PCE using a triple reactant strategy for synthesis and crystal growth<sup>[11]</sup>. Despite currently only possessing half the PCE of the LHPSCs, these tin-based perovskites hold a lot of promise. The tin based PSCs boast multiple improvements in optoelectronic properties as compared to their lead-containing counterparts such as narrower band gaps (1.2 - 1.4 eV), and experimentally higher charge carrier mobilities<sup>[8]</sup>. Furthermore, they have potential applications in flexible single-crystal nanowires<sup>[12]</sup>. The narrower band gap of the Sn PSCs is a massive advantage as the greatest stopgap for the lead PSCs is that their PCE is limited by their larger band gap ( $> 1.5$  eV) according to the Shockley–Queisser (S–Q) limit theory<sup>[13]</sup>. The tin perovskites however do come with their own issues that must be overcome.

Perovskites as a whole struggle with long term stability as a material. They are generally quite sensitive towards oxygen and moisture, and there are many material degradation mechanisms in PSCs such as the decomposition of organic cations, the generation of inorganic byproducts, and more<sup>[14]</sup>. Furthermore traditional PSCs are not resilient to bending and other physical stresses as they are prepared on fragile glass substrates<sup>[15]</sup>. Additional issues that PSCs face are high degrees of polycrystallinity<sup>[11]</sup>, and surface defects<sup>[14,16]</sup> all of which decrease their functional efficiency. These issues are typically corrected using different deposition methods<sup>[11]</sup>, surface passivation<sup>[16]</sup>, and annealing<sup>[17]</sup>. Issues that the Sn based perovskites face uniquely are their low crystallinity (Fig. 3)<sup>[18]</sup>, high prices of tin iodide ( $\text{SnI}_2$ )<sup>[13]</sup>, and the relative instability of the Sn 2+ cation<sup>[6,8,9,13,19]</sup>. The Sn 2+ cation will

readily oxidize to Sn 4+, resulting in self p-doping<sup>[8]</sup>, further reducing the PCE of the solar cells. Because of this, some are altering the other materials such as the electron transport layer (ETL) to decrease the influence of self p-doping rather than preventing oxidation<sup>[19]</sup>.

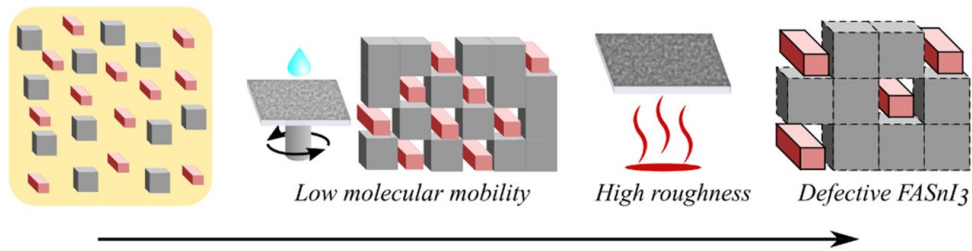


Figure 3: Formation of Highly Defective  $\text{FASnI}_3$  Crystals via Traditional Means. Adapted from (Nasti *et. al.*, 2022).

In this review, the current advancements in the fields of lead halide perovskite solar cells and tin-based lead-free perovskite solar cells are compared and contrasted in the hopes of determining whether or not less toxic materials may one day be as efficient as their lead-based counterparts. Furthermore, the Shockley-Queisser limit theory is discussed regarding a shift to new photovoltaic materials.

## 2 Background

### 2.1 Solar Cells and the Shockley-Queisser Limit

The fundamental technology of solar cells operates on the premise of electron-hole pair (EHP) creation and transport. In the absorber material (commercially c-Si), electrons are excited to higher energy states by high energy solar rays. These excited electrons leave behind electron holes. These electrons and holes then move towards their respective transport layers

via an applied potential difference, creating a depletion layer and subsequently positively charged (p-type) and negatively charged (n-type) layers within the material. The EHP is later recombined across an external load, thus using solar light to perform electrical work<sup>[20]</sup> (Fig. 4)<sup>[21]</sup>.

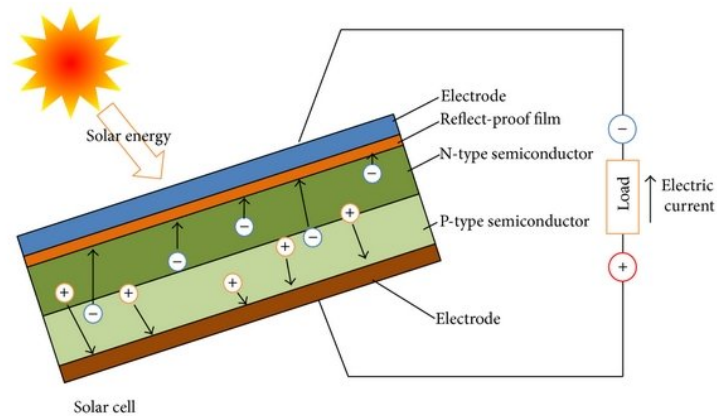


Figure 4: Diagram of Standard Solar Cell Photovoltaic Process. Adapted from (Zhang *et al.*, 2014).

Solar cells are fundamentally limited by what is known as the Shockley-Queisser (SQ) limit theory. The SQ limit theory states a maximum theoretical PCE based on the properties of the material being used, and the spectrum of our sun<sup>[22]</sup>. Crystalline silicon cells only improved in PCE by 1.1% between the years of 2016 and 2020<sup>[23]</sup> marking a significant plateau. The theoretical maximum for these cells is only 33.4%, but is further limited by the low radiative recombination rate in silicon and Auger radiation, capping this technology at 29.4%<sup>[23]</sup>. Auger recombination being the non-radiative process by which the excess energy produced by EHP recombination is transferred to electrons or holes that are subsequently excited to higher energy states within the same band<sup>[24]</sup>, reducing overall efficiency.

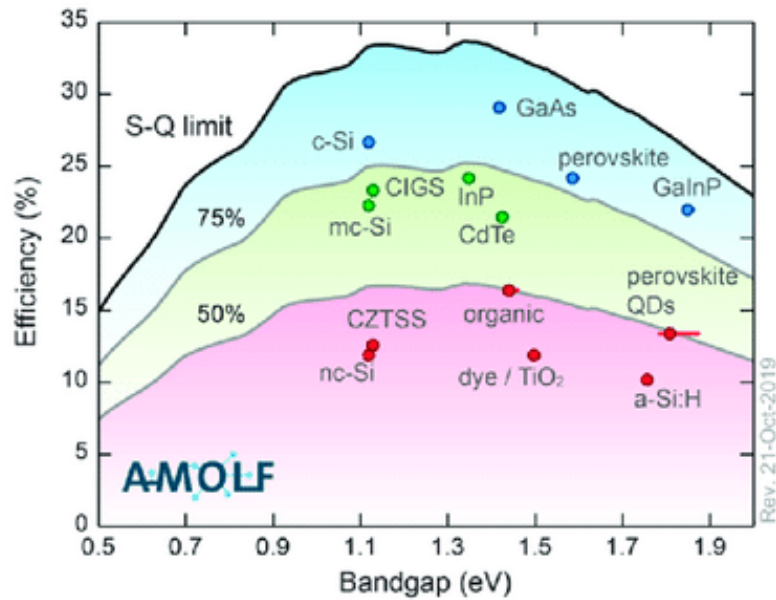


Figure 5: Schematic of Current Photovoltaic Materials, With Theoretical SQ Limit. Adapted from (Brakkee, 2020).

As can be seen in Fig. 5,<sup>[25]</sup> despite being outdated as perovskites have increased in efficiency since this graphic was created, the solid black line represents the theoretical SQ limit set by the emission spectrum of our sun. If a material with a bandgap of 1.2 to 1.4 eV were fabricated, it could have a theoretical maximum PCE of over 33%. This is where tin based PSCs find their niche as a material.

## 2.2 Tin Perovskite Films

With the most common chemical formula being formamidinium/cesium tin triiodide (FA/CsSnI<sub>3</sub>)<sup>[18]</sup>, tin perovskite solar cells are emerging as a promising non-toxic thin-film photovoltaic technology with optoelectronic properties including, but not limited to a highly desirable band gap of 1.2-1.4 eV<sup>[8]</sup> resulting in the highest possible theoretical Shockley–Quisser limit efficiency for single junctions of (>33%)<sup>[11]</sup> (Fig. 5).



### 2.2.1 Synthesis

Perovskites, being crystalline in nature, have been synthesized and grown in many ways to select for specific properties. When used as an absorber in a photovoltaic cell however, they are most useful as crystalline layered films<sup>[3,4,8–12,14–16,18,19]</sup>. The method by which this film is formed varies quite a lot throughout the literature. The current most common way to fabricate the tin perovskite films is to use glass as a substrate on which SnI<sub>2</sub> in dimethyl sulfoxide (DMSO) and formamidinium iodide (FAI) in a cosolvent are placed. The solution is deposited on the substrate, and then the film is annealed<sup>[9]</sup> (Fig. 6). This method however results in the rapid oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup> due to DMSO's oxidizing potential<sup>[11,18,19]</sup>, driving a search for a better solvent. The tin perovskites further suffer from very rapid crystal growth kinetics<sup>[11]</sup>, which makes the film synthesis difficult to control and results in issues such as low crystallinity, low crystal alignment, and high defect rates within the crystal. This high defect rate hinders PCE significantly as it provides trap sites for non radiative recombination, reducing the efficiency of charge transport.

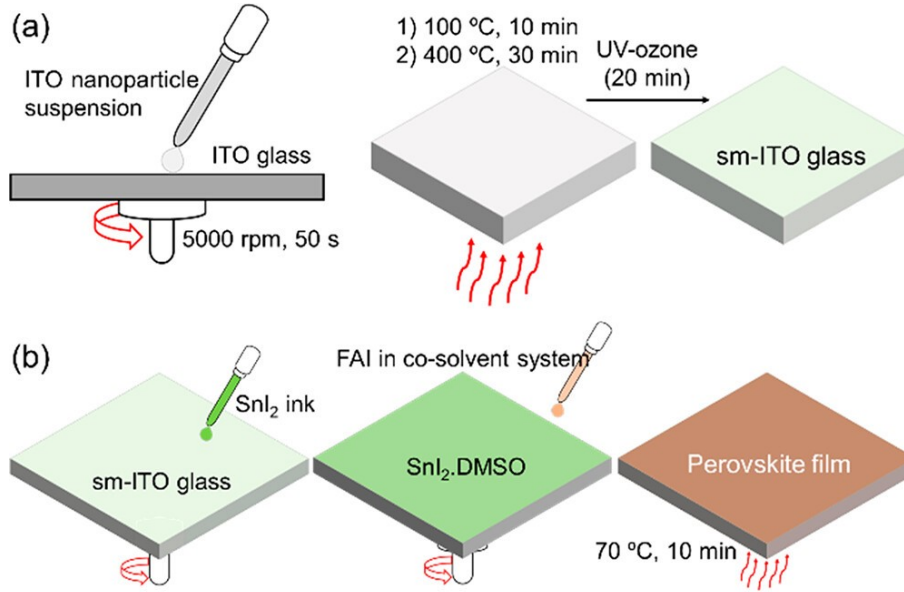


Figure 6: Typical Tin Perovskite Film Synthesis. Adapted from (Rajamanickam, 2023)<sup>[9]</sup>

There has been a lot of research focusing on controlling the growth rate of tin perovskite films (TPFs). Notably, Jiang, *et. al.*<sup>[11]</sup> propose a triple reactant strategy which showed much slower crystal growth as well as much higher crystallinity in their films. As mentioned, TPFs are typically synthesized using a double reactant strategy comprised of SnI<sub>2</sub> and FAI. What Jiang *et. al.* discovered is that the presence of FAI causes the rapid formation of three dimensional (3D) tin perovskites, leading to high defect lattices. To remedy this, the group replaced the FAI with ammonium iodide (NH<sub>4</sub>I) and formamidinium acetate (FAAc). This alteration in reactants resulted in the much slower formation of a low defect quasi-two dimensional (2D) layer. This layer was then used as a template to further construct the 3D perovskite structure, resulting in a more uniform film, with a much smoother surface topology as can be seen in Figs. 8, and 9.

Nasti *et. al.*<sup>[18]</sup> propose a double reactant recrystallization method using tert-butyl pyridine (tBP). In their method, they start with  $\text{FASnI}_3$ , defective  $\text{FAI-SnI}_2$ , and tBP. The tBP allows for higher molecular mobility during the crystallization process, allowing for the removal of both tBP and defective  $\text{FAI-SnI}_2$  in the annealing step (Fig. 7). They report higher levels of crystallinity and alignment, as well as more favourable surface topography.

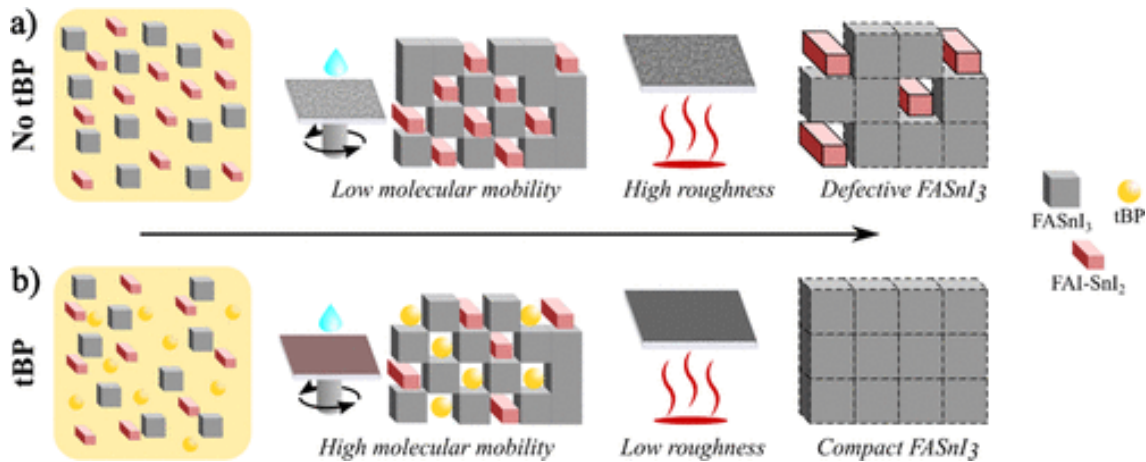


Figure 7: Film Crystallization Method Using tBP Proposed by Nasti *et. al.*<sup>[18]</sup>

### 2.2.2 Characterization

A plethora of techniques are used to characterize PSCs. In terms of perovskite film characterization, xray diffraction (XRD), xray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and grazing incidence wide-angle X-ray scattering (GIWAXS) are widely used methods<sup>[11]</sup>. XRD provides insight as to the structural integrity of the crystals, while XPS is typically used to verify the chemical integrity of the films and make sure that no precursors are present within the film. SEM is incredibly important for the characterization of perovskite films as it gives insight as to the surface topology. Surface interfaces are one of the most important aspects of constructing an efficient solar cell, as these interfaces are in-

tegral to charge transport efficiencies and non radiative recombination reduction. GIWAXS is typically used to determine degree of crystallinity as well as level of crystal alignment, which are very important aspects regarding the efficiency of the solar cell as well, as more homogenous materials will provide higher charge carrier lifetimes, and higher efficiencies.

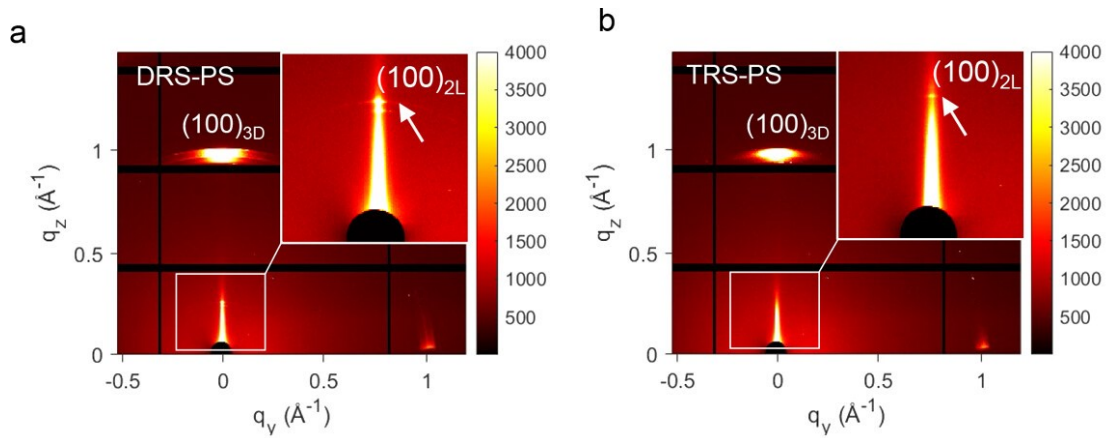


Figure 8: GIWAXS patterns of DRS (a) and TRS (b) films. Adapted from (Jiang, 2023)

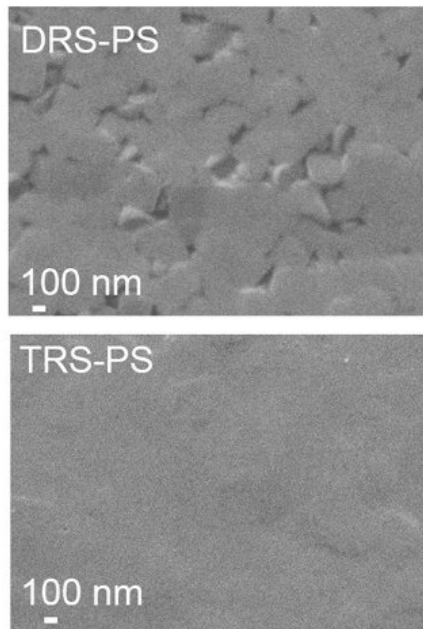


Figure 9: Scanning electron microscopy measurement of DRS and TRS films. Adapted from (Jiang, 2023)

Characterization of the solar cell is typically carried out via current-voltage measurements (I/V)<sup>[14]</sup>, as well as quasi Fermi level splitting (QFLS), photoluminescence quantum efficiency/yield (PQLE/Y)<sup>[26]</sup>, and Time-resolution photoluminescence (TRPL)<sup>[11]</sup>. These measurements are helpful for determining PCE, as well as carrier lifetime and quantum yield, which give important insight to perovskite purity and layer interface compatibility.

### 2.3 CTL and Surface Engineering

Perhaps even more important for optimizing power conversion efficiency of the cells than the perovskite itself are the charge transport layers (CTLs), as well as the interfaces between the perovskite layer and the CTLs. The hypothetical PCE limit of the material is defined by the SQ limit<sup>[22]</sup>, but poor coverage and surface defects can contribute to massive losses in PCE<sup>[27]</sup>, leading to a severe drop in the efficiency of the solar cell as a whole. Because of this, a lot of focus is put on improving the surface chemistry of the perovskite films, as well as improving charge transport efficiency across the CTLs<sup>[6,9–11,14–19,25–27]</sup>. Many different materials are used for the charge transport layers in the field of perovskites, depending on both the surface chemistry of the perovskite and the chemical composition of the transport layer itself. In Fig. 10, Chin *et. al.* test a variety of hole transport layer (HTL) chemistries with a doped and undoped LHP film, in the hopes of increasing the efficiency of the cell. By measuring QFLS, they determine a rough estimate of the power loss due to non radiative recombination<sup>[27]</sup>. Improper contact between the perovskite and charge transfer layers can cause much lower charge mobility and a higher rate of non radiative recombination. The surface of the perovskite and the surface of the CTLs must be compatible to ensure proper charge mobility<sup>[27]</sup>. A common strategy to reduce surface impurities caused by oxidation or

moisture is surface passivation, where the surface is protected by a very thin layer of more inert material, shielding it from the environment<sup>[28]</sup>.

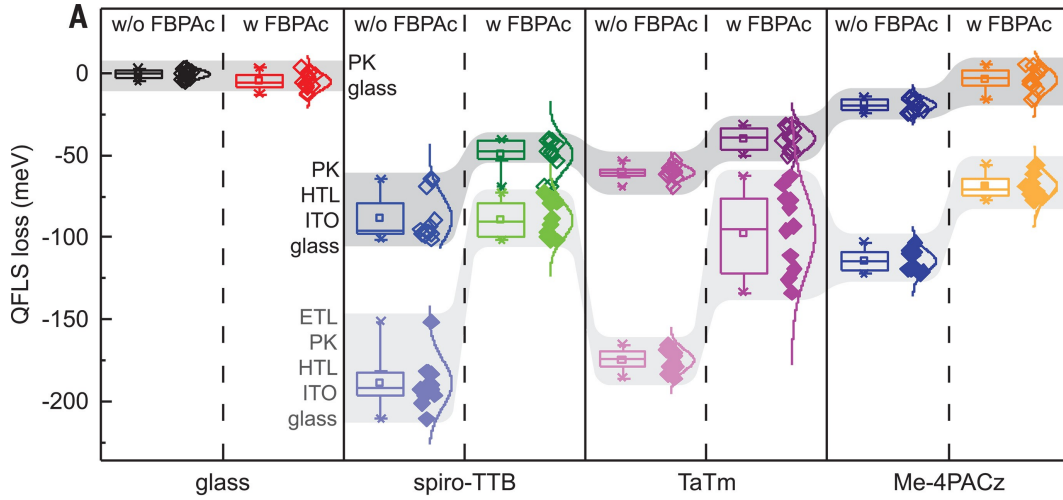


Figure 10: QFLS Measurements on LHPSCs With Different HTL Chemistries. Adapted from (Chin, 2023).

Furthermore, the roughness of the perovskite surface plays a large role in proper layer contact and efficient charge transfer. This is an inherent issue with crystalline films, as most techniques result in high levels of polycrystallinity<sup>[11,27]</sup>. This is an issue as the grain boundaries present as impurities in the crystal, and generate surface roughness that reduces the contact coverage between layers, and generate non radiative recombination sites. Several attempts to remedy this have been made by doping the perovskite and HTL layers<sup>[27]</sup>, as well as slowing down the rate of perovskite crystallization<sup>[9–12,14,15,17,18,27]</sup> to produce smoother surfaces. Miyamoto *et. al.* generate nanoporous interfaces to increase interaction surface area, allowing for higher charge transfer rates, resulting in a PCE of 7% (Fig. 11)<sup>[19]</sup>.

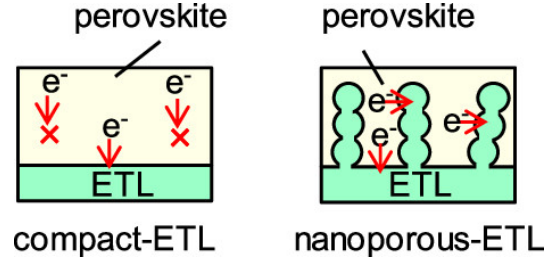


Figure 11: Diagram of Nanoporous ETL/Perovskite Interface. Adapted from (Miyamoto, 2020).

Rajamanickam, *et. al.* sought to remedy the short lifetimes exhibited by traditional tin halide PSCs simply by changing the HTL composition, resulting in a shelf life of over 10000 hours<sup>[9]</sup>. Classically, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is used as the HTL material. This material, while useful as a solar cell HTL, it has many drawbacks such as high acidity, hygroscopicity, anisotropic carrier injection, and photothermal vulnerability that reduce its lifetime greatly. It can be replaced with poly(triaryl)amine (PTAA), however the high hydrophobicity of this material induces non-uniform perovskite film formation, which results in imperfect interfacial connections and a large population of trap sites. Using the typical  $\text{FASnI}_3$  as a perovskite, Rajamanickam, *et. al.*<sup>[9]</sup> use indium tin oxide (ITO) nanoparticle (NP) coated glass as a HTL. The ITO nanoparticles provide nucleation sites for the perovskites, and the surface chemistry of the ITO NPs is easily modified and manipulated to interact favourably with the perovskite using a two step annealing process.

## 2.4 Tandem Cells

By layering multiple photovoltaic materials, one can further improve PCE by constructing a tandem cell, effectively increasing the absorption spectrum range. Lead perovskite/silicon tandem cells have been constructed with hypothetical limits of up to 45.1% PCE<sup>[7]</sup>. As of right now, this technology holds the current highest accredited PCE of nearly 33%<sup>[3]</sup>. Chin *et. al.*<sup>[27]</sup> report the deposition of a LHP layer on micrometric pyramidal c-Si cells to improve photocurrent. Using additive engineering, they control perovskite crystal growth, and alleviate recombination losses at the surface for an accredited PCE of 31.25%. Tandem cells have also been constructed with tin perovskites, with a current highest recorded PCE of 30.7%<sup>[29]</sup>.

## 3 Discussion

Perovskites as a photovoltaic material hold much promise. The explosion in PCE over the last decade has proven as much, considering the stagnation of c-Si technology. The question to answer however, is are they capable of replacing crystalline silicon as a commercial photovoltaic material? Furthermore, can they do so in a way that is not harmful to the environment? The improvement in efficiency afforded by LHPSCs comes at the the aforementioned cost of toxicity. This has sparked a lot of concern surrounding how safe these materials are to use in commercial applications, and rightfully so. If a solar panel were damaged, there would be very little to stop the lead containing perovskites from leeching into the environment. Compared to the current case of c-Si cell breakage, this is much less



safe. Whether this is something that is worth overlooking for the increased efficiency is still highly debated<sup>[8]</sup>, and many are pushing for the commercialization of LHPSCs despite these concerns.

Furthermore, despite solar energy being so abundant, there are very few incentives in place to make the switch to solar or other green energies. Concerns surrounding area of land taken up by solar farms as well as establishment and maintenance costs for the technology exist, however trends show that these costs have been falling incredibly quickly<sup>[30]</sup>. As we learn more about the technology, the operation and maintenance costs of these technologies will only be further reduced. Other issues with solar energy include that the efficacy of solar cells is location dependent, as naturally some places get more sun than others. Ideally, if the conversion efficiency were improved significantly, a smaller area of solar panels would be required, at least partially resolving these issues, and perhaps providing more of an incentive to switch to solar energy.

A lot of hindrance surrounding the switch to greener energy stems unfortunately from the political and financial sectors. Many powerful people rely on fossil fuels such as coal and oil to make money, resulting in a large amount of political lobbying against solar energy incentives<sup>[31]</sup>. Furthermore, people involved in the fossil fuel industry worry about job security in the case of a massive divestment from non renewable energies. Despite these concerns, readily available sources of fossil fuels are dwindling, and the advanced technology required to extract and refine the less readily available sources is contributing largely to greenhouse gas emissions<sup>[32]</sup>. All this being said, is using toxic materials justifiable in our quest for greener

energy?

Perovskites face several issues that have prevented them from commercialization thus far. Many are meeting the required PCEs for commercialization<sup>[3,4,8]</sup>, however their inherent short lifetimes are not sufficient for solar panel use. The issues that they face make them difficult to employ, as solar panels are subjected to physical strain, heating and cooling cycles, and other environmental stresses that perovskites are known to be sensitive to. Many groups have succeeded in alleviating some of these issues, and many groups have been accredited with PCEs higher than those of the commercial c-Si cells, showing the promise of LHPSCs. The technology however has not quite come far enough to supplant the c-Si solar panels. Not all hope is lost however, as PSCs remain relatively new technology, and are constantly evolving and improving at a rapid rate.

Due to the matching 2+ valence shared by the tin and lead ions, tin perovskites are emerging as a very promising non-toxic contender to their better established lead counterparts. These materials have more than just non-toxicity to their name, as they boast multiple improvements over the lead halide PSCs. Their bandgap of 1.2 to 1.4 eV puts them at the highest potential PCE of current single junction solar cell materials as can be seen in Fig. 5 where the Shockley-Queisser limit is shown. The main issues that tin perovskites face uniquely are more rapid oxidation and high defect rates, which lead to lifetime and efficiency shortcomings. Despite these issues, tin perovskites are an even younger technology than the lead based ones, and many groups are already working towards resolving these issues. Additive engineering has already been shown to make significant improvements on the ability to

control the crystal growth kinetics to produce higher PCEs and more reliable films, as well as reduce the rate of oxidation, leading to longer lifetimes.

Furthermore, the oxidation that is exacerbated within the tin PSCs is not unique to them. Lead PSCs suffer oxidation as well and this, along with the lifetimes of the CTLs are large contributors to efficiency degradation over time. If the solar cells cannot operate at above 90% of their initial efficiency on a timescale of years, they simply will not be worth the cost to replace the c-Si cells. This being said, Rajamanickam *et. al.*<sup>[9]</sup> show relatively high efficiency tin PSCs with long lifetimes. Their method yields a PCE of 9.7%, which is relatively good for the current advancements in tin perovskites but is not yet comparable to the lead perovskite PCEs. While this increase in shelf life is promising, the measurements are not representative of the lifetime the cell would have in the field.

The cost benefit analysis of this technology as of right now does not put them in a position to replace the widely used c-Si solar panels<sup>[3]</sup>. Green energies on average have lower operational and maintenance costs than the fossil fuels we currently rely on<sup>[30]</sup>, however the up front costs for implementing such a network are massive. The switch to green energy is a gradual one, and so will be the switch to perovskite solar cells. The timeline on perovskite adoption as a commercial solar cell material will depend ultimately on our energy needs as a species, and as our demands increase some may be compelled to use the toxic lead perovskites, and lead/silicon tandem cells for their already improved PCEs.

The LHPSCs, if implemented, will hopefully be a temporary solution as the technology regarding tin PSCs improves and in theory, will catch up to and even surpass LHPSCs. Tin PSCs, as of now, offer only about half the efficiency of lead PSCs. This however comes as a result of a focus on LHPs in the last decade, whereas tin PSCs have only garnered similar attention relatively recently. Furthermore, tandem cells with a tin perovskite/silicon architecture are already catching up to the lead/silicon tandem cells<sup>[29]</sup>. This could be a significant area of research and discussion as tin PSC PCEs improve, as they theoretically have an even higher maximum PCE than the lead/silicon tandem cells.

## 4 Conclusions

In this review, the current advancements in lead halide PSCs, tin halide PSCs, and tandem cells were outlined with a focus on non-toxic tin halide PSCs. Herein, the plateau of silicon solar cell efficiency was outlined regarding the Shockley Queisser limit, followed by a summary on modern synthesis and characterization of tin PSCs, where a few promising papers regarding these topics were selected and summarized. Furthermore, CTL and perovskite surface engineering were discussed within the scope of reducing non radiative emission as well as expanding device lifetime. The progress in efficiency since the early 2010s was summarized for LHPSCs, tin PSCs, and tandem cells. Solar cell technologies were compared and contrasted to determine prospects for the field of solar energy. Tin perovskites have not yet shown that they are comparable to LHPSCs in terms of PCE, however improvements are rapid.

In conclusion, tin PSCs are not ready for commercial use. They boast multiple optoelectronic improvements as compared to their LHPSC counterparts, but ultimately require massive breakthroughs and improvements in PCE and stability. The outlook on the technology is hopeful nonetheless considering the rapid improvements and high degree of investment from the scientific community. From the selected papers, it is clear that these non toxic materials have a promising future, and significant potential in the development of tandem cells as their PCE rises to match those of the LHPSCs.

## References

- [1] Sutherland, B. R. Solar Materials Find Their Band Gap. *Joule* **2020**, 4 (5), 984–985. <https://doi.org/10.1016/j.joule.2020.05.001>.
- [2] Konagai, M. Present Status and Future Prospects of Silicon Thin-Film Solar Cells. *Jpn. J. Appl. Phys.* **2011**, 50 030001. <http://dx.doi.org/10.1143/JJAP.50.030001>
- [3] Aydin, E. *et. al.* Pathways toward commercial perovskite/silicon tandem photovoltaics. *Science* **2024**, 383 (6679). <https://doi.org/10.1126/science.adh3849>
- [4] Dey, A. *et. al.* State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, 15 (7), 10775–10981. <https://doi.org/10.1021/acsnano.0c08903>
- [5] Shyamal, S., Pradhan, N. Nanostructured Metal Chalcogenide Photocatalysts: Crystal Structures, Synthesis, and Applications. *ACS Energy Letters* **2023**, 8 (9), 3902–3926. <https://doi.org/10.1021/acsenenergylett.3c01236>
- [6] Gu, F. *et. al.* Tin(II) Acetylacetonate as a New Type of Tin Compensator Additive for Tin-Based Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* **2021**, 13 (37), 44157–44164. <https://doi.org/10.1021/acsaami.1c08208>
- [7] Shrivastav, N. *et. al.* Investigations aimed at producing 33% efficient perovskite–silicon tandem solar cells through device simulations. *RCS Advances* **2021**, 11 (59), 37366–37374. <http://dx.doi.org/10.1039/D1RA06250F>
- [8] Wang, M. *et. al.* Lead-Free Perovskite Materials for Solar Cells. *Nano-Micro Lett.* **2021**, 13 (62). <https://doi.org/10.1007/s40820-020-00578-z>
- [9] Rajamanickam, P., *et. al.* Highly Efficient HTM-Free Tin Perovskite Solar Cells with Outstanding Stability Exceeding 10000 h. *ACS Appl. Mater. Interfaces* **2023**, 15 (34), 40700–40708. <https://doi.org/10.1021/acsaami.3c10268>
- [10] Marshall, K. P., *et. al.* Enhanced stability and efficiency in hole-transport-layer-free CsSnI<sub>3</sub> perovskite photovoltaics. *Nat. Energy* **2016**, 1 (16178). <https://doi.org/10.1038/nenergy.2016.178>
- [11] Jiang, X., *et. al.* Highly Efficient Tin Perovskite Solar Cells Based on a Triple Reactant Strategy. *ACS Photonics* **2023**, 10 (6), 1992–1998. <https://doi.org/10.1021/acsp Photonics.3c00471>
- [12] Dai, L., *et. al.* Single-Crystal Nanowire Cesium Tin Triiodide Perovskite Solar Cell. *Small* **2023**, 19 (22), 2208062. <https://doi.org/10.1002/smll.202208062>
- [13] Ran, C., *et. al.* Seeking for Cost-Effective Tin Iodide Source toward Efficient Lead-Free Tin Triiodide Perovskite Solar Cells: Advances and Prospects. *ACS Appl. Energy Mater.* **2023**, 6 (10), 5102–5112. <https://doi.org/10.1021/acsaem.3c00085>

- [14] Lim, K., *et al.* Effect of Interfacial Layers on the Device Lifetime of Perovskite Solar Cells. *Small Methods* **2020**, 4 (8), 2000065. <https://doi.org/10.1002/smtd.202000065>
- [15] Du, D., *et al.* Photovoltaic performance of flexible perovskite solar cells under bending state. *Solar Energy* **2022**, 245, 146-152. <https://doi.org/10.1016/j.solener.2022.08.070>
- [16] Allen, O. J., Kang, J., Wang, Y. First-Principles Study of Group VA Monolayer Passivators for Perovskite Solar Cells. *ACS Appl. Nano Mater.* **2023**, 6 (6), 4279–4287. <https://doi.org/10.1021/acsnm.2c05396>
- [17] Iqbal, Z., *et al.* Unveiling the Potential of Ambient Air Annealing for Highly Efficient Inorganic CsPbI<sub>3</sub> Perovskite Solar Cells. *J. Am. Chem. Soc.* **2024**, 146 (7), 4642–4651. <https://doi.org/10.1021/jacs.3c11711>
- [18] Nasti, G., *et al.* Pyridine Controlled Tin Perovskite Crystallization. *ACS Energy Lett.* **2022**, 7 (10), 3197–3203. <https://doi.org/10.1021/acsenergylett.2c01749>
- [19] Miyamoto, Y. *et al.* High Current Density Sn-Based Perovskite Solar Cells via Enhanced Electron Extraction in Nanoporous Electron Transport Layers. *ACS Appl. Nano Mater.* **2020**, 3 (11), 11650–11657. <https://doi.org/10.1021/acsnm.0c02890>
- [20] Fonash, S.J. Photovoltaic Energy Conversion. In *Solar Cell Device Physics*; Academic Press Inc., 1981; pp 1.
- [21] Zhang, H. *et al.* Photovoltaics: Reviewing the European Feed-in-Tariffs and Changing PV Efficiencies and Costs. *Sci. World J.* **2014**, 2014 (4), 404913. <http://dx.doi.org/10.1155/2014/404913>
- [22] Zanatta, A. R. The Shockley–Queisser limit and the conversion efficiency of silicon-based solar cells. *Results in Optics.* **2022**, 2022 (9), 100320. <https://doi.org/10.1016/j.rio.2022.100320>
- [23] Ehrler, B. *et al.* Photovoltaics Reaching for the Shockley–Queisser Limit. *ACS Energy Lett.* **2020**, 5 (9), 3029–3033. <https://doi.org/10.1021/acsenergylett.0c01790>
- [24] Fu, H., Zhao, Y. Efficiency droop in GaInN/GaN LEDs. In *Nitride Semiconductor Light-Emitting Diodes (LEDs)*, 2nd ed.; Woodhead Publishing, 2018, pp. 299-325.
- [25] Brakkee, R., Williams, R. Minimizing Defect States in Lead Halide Perovskite Solar Cell Materials. *Appl. Sci.* **2020**, 10(9): 3061. <http://dx.doi.org/10.3390/app10093061>
- [26] Dasgupta, A. *et al.* Visualizing Macroscopic Inhomogeneities in Perovskite Solar Cells. *ACS Energy Lett.* **2022**, 7 (7), 2311–2322. <https://doi.org/10.1021/acsnm.3c07903>
- [27] Chin, X.Y. *et al.* Interface passivation for 31.25%-efficient perovskite/silicon tandem solar cells. *Science* **2023**, 381(6653), 59-63. <https://doi.org/10.1126/science.adg0091>

- [28] Kaur, A., Aulakh, J. Study of carbon quantum dots as smart materials for environmental applications. In *Handbook of Nanomaterials for Sensing Applications*; Micro and Nano Technologies, 2021, pp. 223-239.
- [29] Pandey, R. *et. al.* Halide Composition Engineered a Non-Toxic Perovskite–Silicon Tandem Solar Cell with 30.7% Conversion Efficiency. *ACS Appl. Electron. Mater.* **2023**, 5 (10), 5303–5315.
- [30] Steffen, B. *et. al.* Experience Curves for Operations and Maintenance Costs of Renewable Energy Technologies. *Joule* **2020**, 4, 359–375. <https://doi.org/10.1016/j.joule.2019.11.012>
- [31] Graham, N. *et. al.* Carbon Capital’s Political Reach: A Network Analysis Of Federal Lobbying By The Fossil Fuel Industry From Harper To Trudeau. *Can. Polit. Sci. Rev.* **2020**, 14 (1). <https://doi.org/10.24124/c677/20201743>
- [32] Kirsch, S. Running out? Rethinking resource depletion. *Extr. Ind. Soc.* **2020**. 7 (3), 838-840. <https://www.sciencedirect.com/science/article/pii/S2214790X20301829>
- [33] Rong, Y. *et. al.* Challenges for commercializing perovskite solar cells. *Science* **2018**. 361:6408. <https://doi.org/10.1126/science.aat8235>