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ROADMAP

Lead-free perovskites and derivatives for photogeneration: a roadmap to sustainable approaches for photovoltaics and photo(electro)catalysis

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Abstract

This roadmap provides a comprehensive overview of the latest advancements in lead-free perovskite materials for photovoltaic and photoelectrochemical /photocatalytic applications. It highlights the urgent need for sustainable energy solutions, emphasizing the role of lead-free perovskites in addressing challenges related to toxicity, scalability, and efficiency. The roadmap is designed to guide the reader from application-driven perspectives to fundamental materials insights, characterization techniques, fabrication strategies and overreaching sustainability considerations. The document explores key material families, including tin-, bismuth-, antimony-, and copper-based perovskites, detailing their optoelectronic properties, fabrication techniques, and application potential. Special attention is given to advanced characterization methods, green processing strategies, the integration of artificial intelligence and machine learning for material design and optimization and lifecycle impact assessments to ensure environmental sustainability. By bringing together insights from global research communities, this roadmap serves as a strategic guide for advancing lead-free perovskite technology, fostering interdisciplinary collaboration, and accelerating the transition to next-generation solar energy solutions.

Contents

List of Abbreviations

0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AI	Artificial intelligence
AIMD	*Ab initio* molecular dynamic
ALD	Atomic layer deposition
BAAc	N-Butylammonium Acetate
BIPV	Building integrated photovoltaic
ClML	Classical molecular dynamic
CPD	Copper perovskite derivative
CSS	Close-space sublimation
CVP	Chemical vapour deposition
DFT	Density functional theory
DMA	Dimethylammonium
DMAc	N,N-Dimethylacetamide
DMF	Dumethylformamide
DMI	Dimethyl Idosorbide
DMSO	Dimethyl Sulfoxide
EC	Electrolysis
EDX	Energy dispersive x-rays
EELS	Electron energy loss spectroscopy
EOL	End-of-life
ETL	Electron transport layer
FA	Formamidinium
FF	Fill factor
GBs	Grain boundaries
GBL	Γ-Butyrolactone
GHG	Greenhouse Gas
GVL	Γ-Valerolactone
HER	Hydrogen evolution reaction
HOMO	Highest-occupied molecular orbital
HT	High-throughput
HTL	Hole transport layer
IEA	International Energy Agency
IMPS	Intensity modulated photocurrent spectroscopy
IMVS	Intensity modulated photovoltage spectroscopy
IoT	Internet of things
IPV	Indoor PV
I_{SC}	Short circuit current
LCA	Lifecylce assessment
LHP	Lead halide perovskite
LUMO	Lowest-occupied molecular orbital
MA	Methylammonium
MHP	Metal halide perovskite
ML	Machine learning
MLMD	Machine learning molecular dynamic
NAP	Near ambient pressure
nBED	Nano-beam electron diffraction
NMP	N-Methyl-2-Pyrrolidone
PC	Photocatalysis
PCE	Power conversion efficiency
PCS	Photocurrent spectroscopy
PEC	Photoelectrochemical
PIM	Perovskite inspired materials
PLD	Pulsed laser deposition
PSC	Perovskite solar cell
PV	Photovoltaic
PVD	Physical vapour deposition
R2R	Roll-to-roll
RoHS	Restriction on hazardous substances
SECM	Scanning electrochemical microscopy
SOC	Spin orbit coupling effect
STEM	Scanning transmission electron microscopy

SVHC	Substances of very high concern
TAS	Transient absorption spectroscopy
TCAD	Technology computer-aided design
TCS	Transparent conductive substrate
THP	Tin halide perovskites
TPC	Transient photocurrent
TPV	Transient photovoltage
UAV	Unmanned aerial vehicles
V_{OC}	Open circuit voltage
WBG	Wide bandgap
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1. Introduction

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The transition to sustainable energy sources is one of the most pressing challenges of our time. The increasing demand for energy, driven by global population growth and industrialization, has led to a rise in anthropogenic GHG emissions, considerably contributing to climate change. According to the IEA, global energy demand is expected to rise by 25% by 2040, with fossil fuels still accounting for nearly 60% of the energy mix under current policies [1]. To limit global warming to below 1.5 °C, as outlined in the Paris Agreement, a rapid transition to renewable energy sources is imperative. In 2022, global CO_2 emissions from energy reached a record 36.8 gigatons, highlighting the urgent need to accelerate the adoption of sustainable energy solutions [2].

Among renewable energy technologies, solar energy has long been recognized by the research community as the most promising energy source for achieving sustainable energy supply and addressing environmental pollution. The ability to harness sunlight and convert it into usable energy efficiently and sustainably is essential for addressing the increasing global energy demand. PV have emerged as the most rapidly growing renewable energy technology and are already the lowest-cost source of electricity in many parts of the world. In fact, global PV electricity generation surpassed 1000 TWh in 2022, contributing significantly to the decarbonization of the power sector [3]. However, a critical challenge for the future is to scale up PV deployment worldwide. This can be achieved by increasing the efficiency of commercial silicon-based modules. However, silicon based solar cells have already reached power conversion efficiencies close to their theoretical limit in single-junction devices [4]. Thus, new materials must be developed to form multi-junction solar cells or more efficient single-junction alternatives.

While achieving higher efficiencies is crucial, PV technology alone cannot address all energy-related challenges. Many sectors, such as transportation and the chemical industry, still rely on fossil fuels, necessitating the integration of PV materials into solar fuel synthesis. One established route is the coupling of PV devices with EC, where solar electricity powers the electrochemical production of fuels, allowing for modular design and efficient energy conversion [5, 6]. As an alternative approach, PEC and PC systems offer a more direct solution for solar-to-fuel conversion by directly using sunlight to drive chemical reactions, enabling the production of hydrogen through water splitting or the reduction of CO_2 into carbon-based fuels. Table 1 provides an overview of PV, PEC, and PC systems, summarizing their key material requirements, operating mechanisms, and target applications. Coupling PV with PEC systems to form hybrid PV–PEC tandem devices is also becoming increasingly common in the literature, as it allows for optimal use of the solar spectrum [7]. Unlike PV, PEC and PC systems remain at the research and development stage and require significant advancements to reach a real technological level. PV and PC/PEC systems differ significantly in operation, device design, and application scope; however, they all

Table 1. Overview of Solar Energy Conversion Technologies studied in this roadmap: PV, PEC, and PC.

Technology	Input	Output	Mechanism	Key material requirements	Target applications
PV	Sunlight (outdoor PV), light (indoor PV)	Electricity	Light absorption → charge separation → electrical current	Suitable bandgap, high carrier mobility, long carrier lifetime, stability, flexibility (indoor PV)	Power generation
PEC	Sunlight + H_2O (or CO_2)	Solar fuels (e.g. H_2, CO, hydrocarbons)	Light absorption → charge separation → redox reaction at electrode surface	Band alignment with redox potentials, high carrier mobility, long carrier lifetime, stability in electrolyte, catalytic activity (co-catalyst integration)	H_2 generation, CO_2 reduction
PC	Sunlight + H_2O (or CO_2)	Solar fuels (e.g. H_2, CO, hydrocarbons)	Light absorption → charge separation → redox reaction on particle surface	High surface area, co-catalyst integration, band alignment, stability	H_2 generation, CO_2 reduction, environmental remediation

rely on light-absorbing semiconductors, which are the core of all solar-driven technologies. Therefore, their optimization is essential: semiconductors must possess suitable bandgap energies, high charge carrier mobility, and long carrier lifetimes while maintaining stability under operational conditions.

Over the past decade, research efforts have focused on developing novel semiconductor materials with optimized optoelectronic properties for both PV and PEC/PC applications. Traditional materials such as silicon, metal oxides (e.g. TiO_2, WO_3, and Fe_2O_3), and chalcogenides (e.g. CdTe, $Cu(In,Ga)Se_2$) have been extensively studied for their stability and efficiency. However, among the emerging materials, LHPs have gained significant attention due to their exceptional properties, including high absorption coefficients, long carrier diffusion lengths, and remarkable defect tolerance [8, 9]. These attributes make LHPs highly efficient and cost-effective, positioning them as the most promising candidates for next-generation PV technologies and becoming more and more used in PEC/PC technologies. The record PCE of small PV cells has climbed to 27% in 2025 [10], and PV-PEC systems based on formamidinium lead triiodide ($FAPbI_3$) photoanodes coupled with external $FAPbI_3$ PV cells recorded a solar-to-hydrogen efficiency of 9.8% [7]. Despite their potential, LHP-based technologies face critical challenges related to scalability and environmental impact [11]. Most reported LHP-based solar cells rely on non-scalable solution-based fabrication techniques, such as spin-coating, and use toxic solvents like dimethylformamide (DMF), posing significant barriers to large-scale manufacturing [12]. Another major issue is the toxicity of lead, raising regulatory and environmental concerns [13, 14]. While the actual impact of lead in perovskite devices is still debated, the development of lead-free alternatives is essential for ensuring the broader acceptance of perovskite-based technologies.

Luckily, halide perovskites are not limited to the use of lead, but they offer a diverse library of materials whose structural and optoelectronic properties can be tailored through compositional engineering, providing versatility for both PV and PEC/PC applications. The development of lead-free perovskites and derivatives (sometimes called perovskite-inspired materials—PIMs) have become a research hotspot in the last years [12, 13]. Beyond addressing toxicity, lead-free perovskites exhibit unique properties that make them attractive for specific applications. For instance, tin-based perovskites have narrower bandgaps, enabling extended light absorption [14], while bismuth- and antimony-based perovskites possess wider bandgaps, making them suitable for IPV and PEC/PC water splitting (see figure 1 for a schematic diagram of typical values of highly investigated perovskites and PIMs) [15, 16]. The tunability of bandgap and energy level positions is particularly advantageous for PEC/PC systems, which require careful alignment with electrochemical reaction potentials. Nonetheless, it is crucial to demonstrate stability and actual environmental benefits of lead-free alternatives over lead-based perovskites, as materials like tin remain controversial, some studies report potentially higher toxicity to living organisms upon

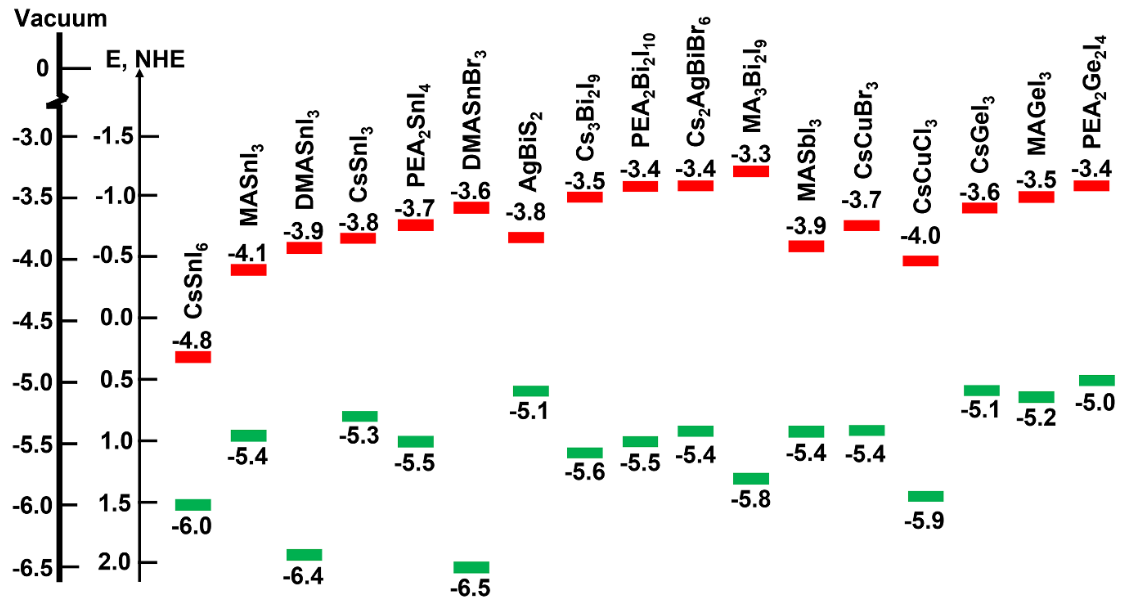
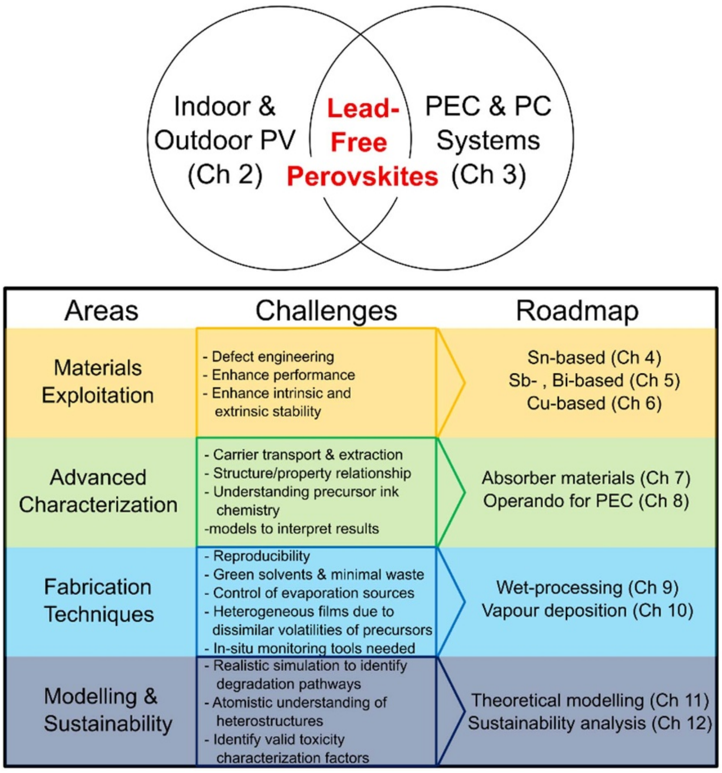


Figure 1. Schematic diagram of energy levels of some of the most studied lead-free perovskites and derivatives (PIMs), namely Sn-based, Bi-based, Sb-based, Cu-based and Ge-based. The valence and conduction bands of each material are indicated with green and red bars, respectively. The potential *vs* the normal hydrogen electrode (NHE) is considered at pH = 0.

environmental release [17], while others highlight reduced bioavailability due to the low water solubility of oxidized Sn^{4+} species [18].

Despite their promise, lead-free perovskites still exhibit significantly inferior performance and stability compared to their LHP counterparts in photogeneration applications [19, 20]. For instance, Sn^{2+} exhibits a strong tendency to oxidize to Sn^{4+}, driving rapid material degradation and compromising long-term stability [21]. To enable their widespread adoption, critical research efforts must focus on enhancing their photoelectric conversion efficiency, developing advanced characterization methods, optimizing green processing techniques for industrial-scale production, and conducting thorough LCA to evaluate resource consumption and environmental impact from raw material extraction to device disposal.

This roadmap provides a comprehensive overview of recent advances and future directions in the field of lead-free perovskites and PIMs, with a focus on their implementation in PV, PEC and PC energy conversion technologies. An infographic outline of the roadmap is given in figure 2. The structure is designed to guide the reader from application-driven perspectives to fundamental materials insights, characterization techniques, fabrication strategies and overreaching sustainability considerations. Chapter 2 opens with the application of lead-free perovskites in both indoor and outdoor PVs, including space, setting the stage with practical demands and use cases that drive material and device innovation. For IPV, the emphasis is placed on materials with optimal bandgaps, integration with IoTs devices and the transition toward lightweight and flexible substrates. For outdoor use, the need for efficient encapsulation strategies and scalable fabrication techniques to enable long-term stability and commercial deployment is highlighted. Chapter 3 introduces PEC and PC technologies, highlighting how insights from PV research can accelerate progress in these complementary solar fuel platforms. Chapters 4–6 delve into three major families of lead-free perovskites: tin-based, bismuth/antimony-based, and copper-based materials, detailing their specific optoelectronic properties, and the trade-offs between reduced toxicity, performance and stability. Chapters 7 and 8 focus on the critical role of advanced characterization in supporting material and device development. Chapter 7 examines techniques to probe intrinsic photophysical limitations in light absorbers, enabling a deeper understanding of material properties-device performance relationship and connecting back to the material challenges discussed in previous chapters. Chapter 8 dives deeper into the importance of operando methods for capturing dynamic processes during PEC operation. These tools provide essential insights into the interplay between structural properties, reaction mechanisms and device stability. The roadmap then transitions to environmentally responsible manufacturing approaches. Chapter 9 addresses green solvent systems for scalable and low-impact film deposition, while chapter 10 presents solvent-free deposition strategies, such as PVD, highlighting how understanding growth mechanisms is key to achieve uniform, high quality films. Chapter 11 shifts to computational tools, discussing how theoretical modelling and AI can accelerate the discovery



Areas	Challenges	Roadmap
Materials Exploitation	- Defect engineering - Enhance performance - Enhance intrinsic and extrinsic stability	Sn-based (Ch 4) Sb- , Bi-based (Ch 5) Cu-based (Ch 6)
Advanced Characterization	- Carrier transport & extraction - Structure/property relationship - Understanding precursor ink chemistry -models to interpret results	Absorber materials (Ch 7) Operando for PEC (Ch 8)
Fabrication Techniques	- Reproducibility - Green solvents & minimal waste - Control of evaporation sources - Heterogeneous films due to dissimilar volatilities of precursors - In-situ monitoring tools needed	Wet-processing (Ch 9) Vapour deposition (Ch 10)
Modelling & Sustainability	- Realistic simulation to identify degradation pathways - Atomistic understanding of heterostructures - Identify valid toxicity characterization factors	Theoretical modelling (Ch 11) Sustainability analysis (Ch 12)

Figure 2. Summary infographic outline of the roadmap, highlighting applications, contributing research areas, and summarizing the main challenges.

and optimization of lead-free perovskites by guiding material design in a targeted, data-driven manner. Finally, chapter 12 concludes the roadmap by examining the environmental sustainability of these emerging technologies, introducing LCA as an unifying framework and calling for the development of new methodologies and toxicity characterization factors tailored to the unique characteristics of lead-free perovskites and PIMs.

Interdisciplinary collaboration will be essential for optimizing PV-PEC coupled systems and advancing artificial photosynthesis, paving the way for more efficient solar energy utilization. By fostering innovation in sustainable perovskite-based materials and devices, this roadmap not only outlines the state-of-the-art in lead-free perovskite research but it also aims to guide the research community in driving the transition toward a more sustainable deployment of solar energy technologies.

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2. Outdoor and IPV applications

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Status

To date, the record PCE of lead-free PSCs is 15.7%, which has been achieved using Sn-based devices [22]. Despite the limited PCE compared with lead-based counterparts, the potential of lead-free PSCs for specific applications in outdoor, indoor and even space environments has attracted enormous interest. Each of these application domains presents distinct operational conditions, performance metrics, and material requirements.

Outdoor PV, typically used in BIPV, ground-mounted, or portable energy systems, demands high PCE, long-term stability under environmental stressors (e.g. UV radiation, humidity, thermal cycling), and scalable manufacturing processes. These applications are subject to standard solar irradiance conditions (AM 1.5G), making thermal and photo-stability primary concerns for material selection and encapsulation strategies.

IPV is designed for low-light environments such as homes, offices, and industrial settings. Here, light intensities are much lower (typically <1000 lux) and spectral distributions differ significantly from sunlight, favouring WBG semiconductors. Lead-free perovskites tailored for IPVs must optimize absorption in the visible range, minimize non-radiative recombination losses, and operate efficiently under artificial light sources such as LEDs or fluorescent lamps.

In-space PVs operate in extraterrestrial environments characterized by vacuum, extreme temperatures, atomic oxygen, and high radiation exposure. While weight and radiation resistance are major priorities, the absence of atmospheric moisture can reduce the burden of environmental degradation. Lead-free perovskites offer the potential for low-cost, lightweight modules with tuneable optical properties and resilience to cosmic radiation, although their in-space reliability is still under active investigation.

By outlining the specific constraints and opportunities of each domain, this chapter aims to highlight the adaptability and future potential of lead-free perovskites for sustainable PV technologies across diverse operational settings.

For outdoor applications, lead-free PSC offer a compelling alternative to mitigate the environmental and regulatory challenges posed by lead-containing devices. Beyond installation in-field or on rooftops, they can be exploited in light-concentrated systems and as integrated semi-transparent PV (e.g. facades, greenhouses), as well as for in-space solar energy harvesting to power satellites and spacecrafts. For concentrated PV and space technology, tandem PSCs are particularly relevant, yielding a higher PCE per unit area and, potentially, a lower cost than other PV technologies (i.e. III–V for space). Lead-based WBG perovskites employed in tandems often encounter stability issues related to halide segregation, which can be avoided in lead-free WBG systems. The presence of different B-site elements can widen the bandgap without using different halides, reducing chemical complexity and manufacturing costs. Currently, the PCE of WBG lead-free PSCs is low but theoretical PCE >30% can be achieved, matching the PCE of lead-based devices [22]. WBG lead-free perovskites are also gaining attention as see-through PV and BIPV, offering reduced light absorption and colour tunability [23]. Since the trade-off between transparency (or colour) and efficiency influences the levelized cost of electricity, efforts to improve their performance are needed.

Interestingly, a considerable number of WBG lead-free perovskites have potentially higher intrinsic stability than lead-based counterparts, since they can crystallize in 2D or quasi-2D (quasi-2D) form [24]. The advantage of enhanced operational stability is often hampered by the limited PCE, due to the presence of organic spacers, acting as an insulating layer. Achieving vertical alignment was demonstrated for lead-based perovskites by hot-casting techniques, which add fabrication complexity and introduce scalability challenges. Instead, some lead-free perovskite crystals can naturally, or through chemical modifications (e.g. chlorine addition in $Cs_3Sb_2I_9$ [25]), adopt vertically aligned 2D structures. This opens up to applications where intrinsic stability is crucial such as wearable devices, greenhouses, or emergency tents. The lightweight nature of these devices could also be advantageous in drone applications UAVs [26]. In such scenarios, it is essential to characterize these systems under diffuse radiation conditions, e.g. cloud albedo or overall land albedo, while also assessing their bifacial capabilities.

Unlike outdoor PV, IPV operate under artificial lighting, where light intensity is much lower, and stability challenges differ from those posed by harsher outdoor conditions. Lead-free perovskites have demonstrated promising PCE under indoor lighting conditions, with tin perovskites delivering 20.12% PCE under 1000 lux (white LED) [27]. Their high absorption coefficients and suitable bandgaps (1.7–2.0 eV) for optimal spectral matching with common indoor light sources, i.e. LEDs and fluorescent lamps, make them ideal candidates for indoor energy harvesting, ensuring also enhanced environmental stability and lower toxicity, compared to traditional lead-based perovskites.

If deployed on flexible substrates, their superior mechanical flexibility and compatibility with solution-based fabrication techniques can enable miniaturization and seamless integration and make them highly attractive for powering low-energy electronics, such as IoT devices, smart packaging, wireless sensors, wearable and miniaturized autonomous systems [28].

Current and future challenges

Despite the recent promising advances and theoretical calculations based on the Shockley–Queisser limit, suggesting $>30\%$ PCE for lead-free PSCs [29], achieving high PCE for this class of perovskites remains a critical challenge [28].

As main competitor, lead-containing perovskites, particularly those based on methylammonium and formamidinium lead halides, have achieved record PCE exceeding 27%, primarily due to their exceptional optoelectronic properties, including high absorption coefficients, long carrier diffusion lengths, and benign defect tolerance properties. The elemental lead genome properties, i.e. the suitable ionic radius, the spin–orbit coupling effect (SOC), and the unique atomic electronic configuration can be considered as the origin of these superior optoelectronic properties [30]. In particular, the high optical absorption capability of lead-based perovskite has been imputed to the combination of the direct band gap and P–P transitions, ensured by the unique electron configuration of lead [31]. Regarding the abnormal long carrier diffusion length, which has been experimentally found to exceed 1 μm in $MAPbI_3$ (MA = methylammonium), the reasons must be sought in the Pb electronic configuration and the strong SOC effect. Indeed, on one side, a strong s–p coupling is occurring at the valence-band maximum between the Pb 6 s orbital and the halogen p orbital, inducing a small effective mass of holes. On the other side, the strong SOC effect contributes to the small electron effective mass by inducing a large splitting in the conduction-band maximum [32]. The small effective mass of lead-based halide carriers ensures unusually long carrier diffusion lengths to the perovskite films. Finally, regarding the defect tolerance of lead-based perovskites, several studies unequivocally demonstrated that the wrong bonded or anti-bonded states have high energy making them extremely unstable. Thus, unlike traditional semiconductors, most of the point defects in the lead-based perovskites only originate shallow levels. Moreover, differently from the other polycrystalline semiconductor absorbers, the influence of structural defects related to the GBs on lead-based PSCs is negligible [33]. Yin *et al* demonstrated by DFT calculation that the typical large lattice constant in lead-based perovskite avoids the generation of cation–cation and anion–anion wrong bonds [34]. Thus, the defects formed at the GBs are mainly caused by Pb and I dangling bonds, Pb–I–Pb mis-bonding angles and redundant bonds (Pb_2), all of these originating shallow defect levels. Therefore, the effect of a large lattice constant in relaxing the lattice structure and weakening the wrong bands at GBs, confers to the lead-based perovskite an astonishing defect tolerance behaviour.

In contrast, lead-free perovskites—such as tin-, bismuth-, antimony-, and copper-based compounds—generally exhibit lower efficiencies due to issues like increased defect density, rapid oxidation (e.g. Sn^{2+} to Sn^{4+}), poor film morphology, or unfavourable band structures. In addition, the absence of lead introduces structural instability, compromising the material's ability to sustain optimal electronic properties under operational conditions. Moreover, many lead-free materials struggle with sub-optimal bandgap alignment between the perovskite absorber and the charge transport layers, which can result in increased recombination losses and reduced photon harvesting efficiency. These factors contribute to lower open-circuit voltage (V_{OC}) and FF, ultimately reducing the overall device efficiency. Strategies such as compositional engineering, defect passivation, and use of low-dimensional structures have shown promise in mitigating these limitations.

Among the lead-free perovskite technologies showing the most promising PCE, Sn-based PSCs showed max PCE approaching 16% under full sun light [35] and up to 20.12% in indoor (white LED, 1000 lx) conditions [27]. The reduced PCE is commonly imputed to the high V_{OC} losses caused by increased recombination from defects like Sn^{2+} and Sn^{4+}, which are triggered by oxidation and raise background carrier density. Additionally, rapid crystallization leads to small grains and pinholes, increasing recombination at GBs and interfaces, thereby reducing device performance. Similarly, the maximum

PCE reached by bismuth-based solar cells stops at values slightly above 10% reached by a Cs-based quaternary sulphur halide $CsBiSCl_2$ perovskite [36]. Here, the major concern regarding the solubility of the Bi_2S_3 was solved by introducing N,N-Dimethylacetamide (DMAc) in the precursor solution, forming a $DMAcBiS_2$ intermediate with good solubility. However, the limited charge transport, the high defect densities, and the not optimized perovskite film quality are key factors still hampering the PCE of $CsBiSCl_2$ devices. Also bismuth-based perovskite derivatives, such as double perovskite ($Cs_2AgBiBr_6$, max PCE = 6.37%) [37] and vacancy-ordered perovskite ($Cs_3Bi_2I_9$, max PCE = 3.6%) [38], demonstrated still limited performance due to their poor charge transport properties.

From here, it is clear that lead-free perovskites offer significant potential for improvement through strategies such as compositional engineering, dimensionality tuning, and interface optimization.

Moreover, in specific applications—such as IPV or flexible electronics—where toxicity, stability, or low-light performance is prioritized over absolute efficiency, lead-free materials may eventually compete with their lead-based counterparts [39]. Continued research into these materials is essential to unlocking their full potential while aligning with environmental and regulatory demands.

Ongoing research is focused also on optimizing the processing techniques for these materials, while developing a device structure that ensures proper energy level alignment and charge extraction at the electrodes [40], but further progress is needed to reach performance levels required for commercialization.

Manufacturing scalability poses additional challenges, especially in balancing material processability with environmental and human safety. While lead-free alternatives are actively explored to address toxicity concerns, some of the candidate elements, such as Sn and Ge, still exhibit significant toxicity, and some others, e.g. Sb and Bi, require careful assessment of their impact during large-scale manufacturing and deployment.

The extensive yet common utilization of toxic and hazardous solvents for the device fabrication, e.g. DMF, DMSO, N-methyl-2-pyrrolidone (NMP), calls for stringent safety protocols to protect the personnel involved in the manufacturing. Notably, DMF has been prohibited in Europe as of 2023, with the potential for similar restrictions to be implemented in other regions in the near future. Consequently, there is an urgent need for the development of more environmentally friendly methodologies to mitigate the associated health and environmental risks during the fabrication. Research into alternative solvents, including water, ethanol, triethyl phosphate, and γ-valerolactone (GVL), aims to reduce toxicity and improve environmental compatibility. Among these solvents, triethyl phosphate has demonstrated the most promise, enabling the fabrication of uniform, high-quality tin-based perovskite films with improved stability, while water-based processing has also shown feasibility for low-temperature deposition of eco-friendly PSCs [41].

Moreover, transitioning from lab-scale fabrication to industrial-scale manufacturing demands cost-effective and industrially viable manufacturing processes, reproducibility across large areas, compatibility with HT R2R printing techniques, and long-term operational stability—all of which must be achieved without compromising environmental sustainability. Indeed, establishing manufacturing protocols for lead-free solar cells that ensure reduced environmental and health risks is crucial for transitioning production from a purely research-oriented phase to an industrial one.

Equally important is demonstrating the long-term stability of these cells under various operational conditions [42]. Therefore, it is imperative to first establish a set of stress test protocols for these emerging technologies and then customize them for specific applications. Currently, there is a lack of outdoor durability tests for both semi-transparent and opaque cells and modules, as well as evaluation under highly ionizing radiations, such as gamma rays or charged particle beams, which are critical for space applications.

Further advances will unlock significant benefits, including enhanced sustainability, improved device longevity, and wider commercial applicability, especially if the transfer from rigid and heavy glass to lightweight flexible substrates is successful. Continued research in material engineering, encapsulation strategies, and scalable fabrication methods will drive the transition of lead-free perovskites from lab-scale demonstrations to market-ready solutions.

Advances in science and technology to meet challenges

To address the challenges associated with lead-free PSCs, significant advancements are required across multiple scientific and technological domains.

The sustainability of materials and processes is a crucial topic and must be continuously assessed, favouring LCA analysis [39], and improved. A shift towards non-toxic precursors and solvents, low-waste and low temperature fabrication methods, and recyclable components is key in making lead-free perovskite technology not only high-performing but also environmentally viable. A holistic approach is required, encompassing environmentally benign material selection, scalable and low-cost fabrication processes, and energy-efficient manufacturing techniques. Life cycle impact, resource availability, and EOL recyclability are also critical factors shaping materials and process choices. These criteria must be met without compromising the optoelectronic performance and long-term stability of the devices.

One of the most critical areas of development lies in materials formulations. The oxidation sensitivity of tin-based perovskites, for example, can be mitigated through the strategic incorporation of dopants and stabilizing agents. By fine-tuning the chemical composition, it is possible to enhance the intrinsic oxidation resistance of these materials, thereby extending their operational lifespan. Recent studies suggest that additives such as reducing agents or passivating molecules (e.g. thiol-based compounds, bidentate ligands) can effectively suppress the oxidation of Sn^{2+} to Sn^{4+}, improving charge carrier dynamics and overall device stability [43, 44]. Similarly, alloying strategies, where elements like germanium, bismuth, or antimony partially replace tin, can contribute to improved environmental robustness while preserving favourable optoelectronic properties [45]. Further progress can be achieved through AI-driven discovery and optimization. Al-assisted material selection has emerged as a promising route to modulate optoelectronic properties while maintaining structural stability. Incorporation of small amounts of aluminium into the perovskite framework has shown potential to passivate defects and reduce trap density, complementing earlier advances in cation/anion tuning and heterostructure design. When integrated into material design workflows, such alloying approaches can accelerate the development of efficient and stable lead-free compositions. ML-assisted material screening can accelerate the identification of novel lead-free perovskite compositions with superior optoelectronic properties, stability, and performance. AI models trained on HT experimental and theoretical datasets can predict promising material candidates and guide the synthesis of perovskites with tailored properties [46].

For Sn-based perovskites, the well-known fast oxidation from Sn^{2+} to Sn^{4+} significantly limits their terrestrial applications, unless robust encapsulation strategies are implemented. In contrast, they may be more suitable for space applications, where oxidation is less of a concern in oxygen-deficient environments. Further studies on the radiation tolerance of high-efficiency lead-free perovskite devices are necessary to explore their feasibility in space environments [47].

Beyond materials chemistry, advances are also needed in adapting materials and processes for flexible substrates. Lightweight, rollable, and even stretchable devices require deposition techniques compatible with flexible platforms such as plastic films, metal foils, or textiles. The use of flexible substrates is crucial for enabling next-generation PV applications, including wearable electronics, integrated energy solutions, and large-scale R2R manufacturing, which can significantly reduce production costs and expand the application possibilities of lead-free perovskites [48]. This needs the use of scalable deposition processes, including blade coating, slot-die printing, and spray coating, ensuring they are optimized for low-temperature fabrication to prevent substrate damage [49]. Additionally, flexible substrates demand enhanced mechanical stability, which can be achieved through strain-engineered interfaces or the incorporation of elastomeric layers that absorb mechanical stress and reduce crack propagation [50].

Effective encapsulation strategies play a unique role in ensuring long term stability. Advanced encapsulation methods, such as ALD barrier coatings, and hybrid organic-inorganic encapsulants are being explored to protect devices from moisture and oxygen ingress [51]. Additionally, self-healing encapsulants, which can repair microscopic defects, represent an emerging frontier in maintaining long-term device durability [52].

Establishing consensus around standardized testing protocols is another pressing need. Current stability assessments often vary across research groups, making it difficult to compare results. However, efforts are underway within the research community to address this issue, as highlighted by recent initiatives advocating for unified stability testing frameworks and reporting guidelines [53–55]. A standardized approach should not only include well-established indoor characterization methodologies but also encompass long-term operational stability tests under realistic environmental conditions, including humidity, thermal cycling, and photostability tests under continuous illumination. Moreover, the development of accelerated aging protocols will be crucial to simulate multi-year exposure within shorter timeframes, helping to predict real-world device performance.

These interdisciplinary advancements will collectively drive the next generation of lead-free perovskite solar technologies toward industrial adoption, ensuring their competitiveness in the broader PV market (see figure 3).

Concluding remarks

Advancements in lead-free perovskite technology are paving the way for more sustainable and commercially viable PV solutions, going from both outdoor and indoor applications. The transition from heavy, rigid glass to lightweight, flexible substrates is a critical step toward enabling scalable and adaptable PV

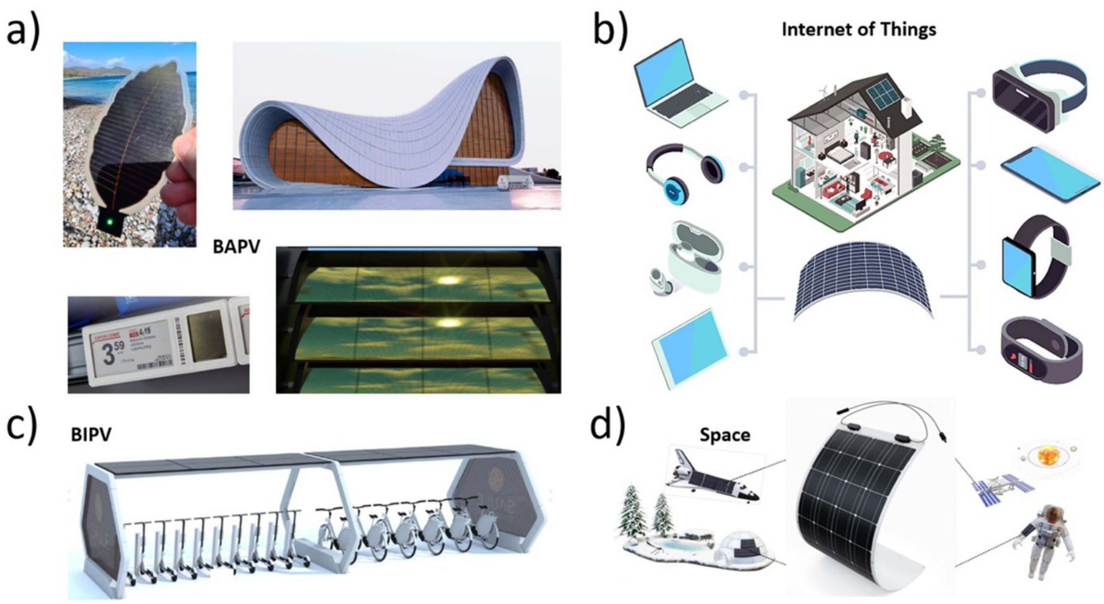

Figure 3. Potential application of lead-free flexible perovskite solar technologies: (a) building applied photovoltaic application (BAPV), with free form design, adaptable to any building. *Source*: Saule Technologies (b) Internet of Things application, with potential use of perovskite-based flexible photovoltaics as a substitute or powering up battery technology in the portable devices present in residential home and for personal use, like smartphones, smartwatches and smart bands, portable laptops, wireless headphones and virtual reality googles. *Source*: IDTechEx Research; (c) building integrated photovoltaics (BIPV), with integration of flexible solar product in buildings and specific instalment, harvesting energy from windows and facades to power up electrical cars, scooter and bike sharing, such as a carport station; *Source*: Saule Technologies; (d) flexible solar technology for space and polar environment, due to its lowest power to weight ratio and better performances under low temperature. [48] John Wiley & Sons. © 2025 Wiley-VCH GmbH.

systems. These innovations will enhance mechanical durability, portability, and energy efficiency, making lead-free perovskites highly attractive for applications such as BIPV, IoT, wearable electronics, and autonomous energy systems.

For outdoor applications, improved encapsulation techniques will be essential to ensuring long-term operational stability under harsh environmental conditions, including moisture, UV exposure, and temperature fluctuations. Meanwhile, in indoor environments, continued research in low-light energy harvesting will allow lead-free perovskites to be seamlessly integrated into IoT networks, smart sensors, and electronic devices that rely on artificial lighting.

Further development in large-scale fabrication methods, such as R2R processing and solution-based deposition, will drive down production costs while increasing the accessibility of lead-free perovskite PVs. By addressing these challenges, lead-free perovskites are positioned to become a key player in next-generation sustainable energy solutions, minimizing dependence on toxic materials while meeting the increasing global demand for clean energy.

Acknowledgments

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3. PEC and PC with lead-free halide perovskites: lessons learned from PVs

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Status

PEC cells have gained considerable attention since the pioneering study by Honda and Fujishima in 1972, which demonstrated oxygen evolution on TiO_2 anodes upon ultraviolet light irradiation. Since that discovery, research has focused on achieving good solar light absorption, efficient generation and transport of non-equilibrium electrons and holes, good stability, and low toxicity in semiconductor-coated photoelectrodes for PEC systems. Over the years, many promising semiconductors for PEC and PC applications have been identified, supported by parallel advances in PV absorber materials [56]. However, high solar fuel and chemical production using low-cost, high-quality, and non-toxic semiconductors in PEC and PC devices remains a persistent challenge.

Metal oxide perovskites such as Al-doped $SrTiO_3$ have demonstrated excellent optoelectronic properties for PC applications but poor absorption of the solar spectrum. Other oxide perovskites offer wider solar spectrum absorption but high density of defects [57]. In contrast, MHPs exhibit key features of an ideal photoabsorber, offering tremendous potential for both PEC and PC applications. Their remarkable solar light absorption, which contributes to photocurrent generation, ability to generate high quasi-Fermi level splitting under illumination, which translates to photovoltage, and defect tolerance, which helps reduce charge recombination, make them excellent candidates for these applications. The wide range of available compositions also covers a wide set of band-edge energy levels, making them adaptable for various targeted reduction and oxidation reactions [58]. However, the general instability of MHPs in aqueous media and the presence of Pb^{2+} in traditional ABX_3 perovskite structures raise toxicity concerns and limits their broader application. These issues have motivated the research of lead-free MHPs and, consequently, several interesting lead-free compounds have been developed with bandgaps ranging from 1.3 to 3.0 eV, as shown in figure 4(a) [59]. The successful development of stable lead-free MHPs with properties comparable to traditional lead-based MHPs would represent a major breakthrough for solar fuel and chemical production technologies.

The general approach has been to substitute Pb(II) at the B site with divalent metals such as Sn(II) and Ge(II) or with a monovalent and trivalent metal such as Ag(I) and Bi(III) or Sb(III) to form double perovskites. Other strategies include creating low-dimensional, vacancy-ordered structures of $A_2B^{IV}X_6$ with tetravalent metal Sn(IV) or Ti(IV). In addition, substituting the B site with trivalent metals such as Bi(III) or Sb(III) in $A_3B_2X_9$ structures leads to 0D and 2D polymorphs [60]. There is also growing interest in non-perovskite structures, such as Rudorffites or pnictohalides (Ag_3BiI_6, Ag_2BiI_5, $AgBiI_4$, $AgBi_2I_7$) [61].

Current and future challenges

Despite sustained research efforts, the performance of lead-free PV devices remains significantly lower compared to lead-based counterparts, in terms of both photovoltage and photocurrent, as illustrated in figure 4(b). Consequently, only limited progress has been achieved in PEC and PC systems. The primary limiting factors include the oxidative instability of the B-site ion due to the absence of lanthanide shrinkage (i.e. the absence of orbital contraction caused by 4f electrons makes it easier for e.g. Sn to lose its 5s electrons, whereas in lead-based perovskites the contracted 6s orbital keeps these electrons more inert) [62], low dimensionality that results in high exciton binding energy and wide optical bandgap, a strong tendency to form structural defects that introduce energy states within the bandgap, inefficient carrier separation, and strong interactions with the lattice (polaron) causing charge carrier localization and recombination, known as self-trapping effect [40, 63].

Mostly WBG (>2.0 eV) lead-free MHPs have been found to exhibit certain stability for solar fuel and chemical production, primarily in PC studies. For instance, $Cs_2AgBiBr_6$ and $Cs_3Bi_2X_9$ (X: Br, I) have shown promising activity and stability in alcohol-based systems and/or in heterojunctions [64–68], while $DMASnBr_3$ has demonstrated performance in aqueous media [69]. Enhancing the spectral tunability of

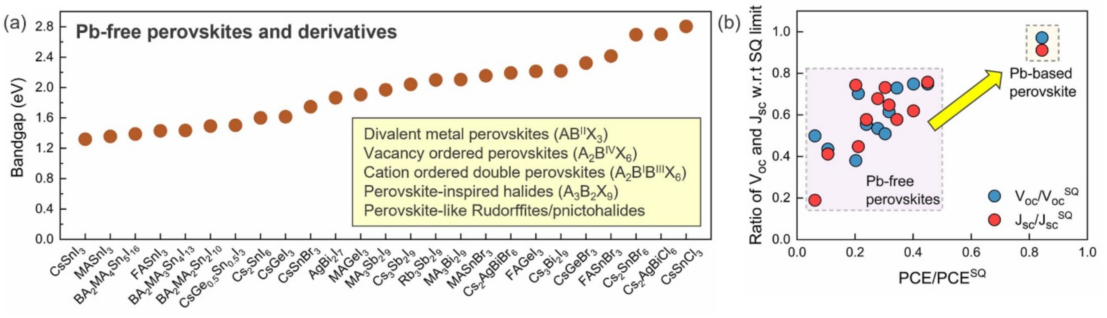

Figure 4. (a) Bandgap of various lead-free compounds that are suitable for solar cells and photoelectrochemical cells. (b) Normalized performance metrics of lead-free MHP based photovoltaic devices. Data for record efficiency lead-based MHPs based standard photovoltaic device is shown for comparison.

these compounds is necessary to improve optical absorption, while addition of co-catalysts can enhance yields and selectivity. Among low bandgap perovskites, mainly Cs_2SnI_6 and Cs_2CuBr_4 have demonstrated functionality in PC systems [70, 71]. Given the range in bandgaps, forming charge selective heterojunctions such as Z-schemes [72] with suitable bandgap combinations would be an effective strategy to maximize optical absorption while enabling strong redox potential.

Initial evaluation of many compositions, as in the case of PVs, can be carried out using drift-diffusion simulations, in a specific architecture, that incorporate the known recombination pathways for the specific compound. This approach can also help in selecting appropriate compositions that are most suitable for PEC and PC applications, allowing researchers to prioritize them for further study. Even when high-performing lead-free MHPs are achieved, chemical stability under illumination and in contact with electrolytes or reactants remains a critical challenge. Innovative corrosion mitigation strategies, inspired from concurrent developments in lead-based MHPs, such as carbon layer protection, may extend operation lifetimes [73]. These persistent issues explain why PEC studies on lead-free MHPs remain limited, and why only a few examples of PC operation exist. Additionally, the absence of standardization of PC device testing presents a challenge for making valid comparisons.

Advances in science and technology to meet challenges

There is a significant performance gap between lead-based and lead-free MHPs. The key challenge, therefore, is to implement effective strategies that can substantially enhance the optoelectronic properties of lead-free compounds. Modified device structures such as those incorporating organic or inorganic transport layers (i.e. mesoporous TiO_2) or nanostructuring can help alleviate transport limitations associated with the low charge diffusion lengths of lead-free MHPs. For compositions with high defect densities and poor stability, molecular passivation strategies and dimensionality tuning (via doping, substitution, or layer stacking) developed for PV devices can be adapted. For example, the hydrogenation of $Cs_2AgBiBr_6$ can lower its bandgap from 2.18 to 1.64 eV, achieving 6.43% PCE with good environmental stability [37]. Mechanistic studies of photo-chemical degradation using spectroelectrochemical and *in-situ* techniques have proven valuable in other PEC systems [74]; applying these methods and techniques to lead-free MHPs will be essential in rationally addressing their intrinsic limitations.

The integration of perovskite PV structures into PEC cells or devices without forming a semiconductor/liquid junction is a promising strategy to overcome the stability challenges of perovskites in aqueous electrolytes. This can be realized by employing n–i–p structures for anodes and p–i–n structures for cathodes, together with protective impermeable layers made of materials such as carbon allotropes, metal films, or resins, as well as catalysts for oxidation and reduction reactions, all either wire-connected or monolithically integrated into compact devices [73, 75, 76]. Such integration allows PEC systems to benefit from PV expertise and to rapidly transfer advances in PV technology and electrocatalysis to PEC applications in a modular manner. In addition, this device engineering can exploit photothermal coupling among the components to enhance performance, for instance by accelerating reaction kinetics [77].

Device architectures that support a broader range of catalytic reactions are also desirable. In this context, even though high bandgap MHPs may appear unsuitable, they can be combined with low bandgap materials to construct tandem Z-scheme architectures to extend application scope, from conventional reactions such as H_2 evolution and CO_2 conversion to valorization reactions such as organic transformations, for example glycerol waste valorization [78, 79]. The combined larger photovoltage achieved in a tandem device can be used to drive more demanding multi-electron reactions in a standalone manner.

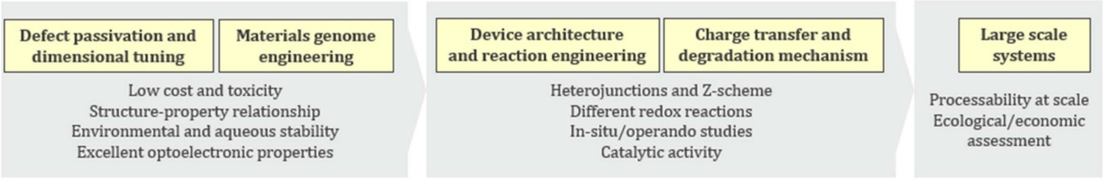

Figure 5. A possible roadmap summarizing the efforts required for lead-free MHP based PEC and PC development.

Although several compositions have been reported and many more to come, a truly efficient and stable lead-free MHP has yet to be identified. The expanding composition library highlights the need for rational design and selection criteria that go beyond empirical approaches based solely on bandgap and band-edge positions. The complexity of the multidimensional parameter space and the need for simultaneous property optimization can be addressed using advanced materials genome engineering, which combines HT experiments, database inputs, and AI. It is urgent to implement such materials discovery strategies to accelerate progress in lead-free MHPs for PEC and PC technologies. A potential roadmap to guide this development is presented in figure 5.

Concluding remarks

Lead-free MHP-based PEC and PC systems are still at an early stage in the field of solar fuel and chemical production. Although significant efforts have resulted in the development of many promising compositions, major breakthroughs are still required to produce lead-free MHPs that are both stable and highly active. Advances made in PVs can be adapted for rapid material screening and for implementing effective surface passivation strategies. Narrowing the PV performance gap between lead-free and conventional lead-based MHPs will help set a benchmark for PEC and PC devices. Therefore, insights from PV research will continue to play an essential role in tuning material properties via doping or dimensional modifications. Ongoing progress in computational and AI-driven materials discovery can also accelerate the development of novel compounds, either from existing libraries or through the design of entirely new compositions. There exist ample opportunities to study mechanistic aspects of charge transfer and degradation processes. If current challenges are resolved, these materials could become a frontrunner in solar fuel and chemical production. It remains uncertain whether a balance between performance and toxicity will be achieved through the development of lead-free and lead-based MHPs that perform well. Addressing this complex problem will require concerted interdisciplinary efforts across chemistry, physics, theory and data science.

Acknowledgments

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4. Tin-based perovskites and the role of defects

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Status

THP are an emerging class of semiconductor materials which have tremendous potential across different energy applications. Similar to their lead-based counterparts, THPs can be easily tuned in terms of optoelectronic properties, bandgap, and band energy positions by adjusting the chemical composition. This versatility makes them particularly suited for both PV and PC applications. Depending on the target application, different compositions and structural motifs of THP are preferred.

In PV, the most effective THP materials adopt a 3D ABX_3 perovskite structure, typically incorporating FA^+, MA^+, Cs^+, or a combination of these as A-site cations, Sn^{2+} as B-site and I^- as primary halide in the X-site (figure 6(a)). A key advantage of these materials is their tuneable bandgap, which can be optimized to 1.3–1.35 eV [80], close to the Shockley–Queisser limit for single-junction solar cells, allowing for highly efficient light absorption. Since the first report of THP in 2014 [81], their PCEs have improved significantly, reaching a certified 15.7% [35]. This progress stems from advancements in film formation [82], material composition engineering [82, 83], interface passivation [84], and the development of optimized charge transport layers [85]. Given that the highest reported PCE is still only about half of the theoretical limit, further research is essential to push THP-based solar cells closer to their full potential. THP materials currently demonstrate the highest performance in PV devices among the lead-free compositions. The next most promising class is the double perovskite family, such as $Cs_2AgBiBr_6$, which however exhibits a considerably less efficient PV response, with a record PCE around 6.4% [37]. These lower efficiencies are mainly due to intrinsic material limitations such as an indirect bandgap, limited solubility in conventional solvents, and a high density of deep defects, which accelerate non-radiative recombination [86].

For PC, wider-bandgap THPs are preferred to ensure sufficient driving force for the redox reactions to proceed efficiently. These include both ABX_3 perovskites with DMA^+ as the A-site cation, such as $DMASnI_3$ and $DMASnBr_3$ (figure 6(b)) [69, 87–89], and vacancy-ordered double perovskites, such as Cs_2SnBr_6 (figure 6(c)) [90–93]. These materials exhibit bandgaps ranging between 2.5 and 3 eV and have energy band positions that make them suitable for photocatalytic applications such as water splitting, CO_2 reduction and N_2 photofixation. Additionally, their superior moisture stability compared to lead-based perovskites is a crucial advantage [94–96], as catalytic processes often occur in humid or aqueous environments. Despite promising initial results, current THP-based photocatalytic systems have only demonstrated activity for short durations (typically under four hours), highlighting the need for further research to improve their long-term stability and efficiency.

Current and future challenges

A critical aspect of THP materials in both PV and PC applications is the role of defects, which can either enhance or limit performance depending on their nature and distribution. Given this duality, it is essential to clarify which defects are beneficial and which need to be mitigated for each specific application.

In PV, the key challenge lies in the intrinsic self-p-doping of THP, which originates from the low formation energy of Sn vacancies [80]. These vacancies create shallow acceptor states, leading to high background carrier concentrations that severely limit carrier lifetimes and charge extraction efficiency (figure 6(d)) [97–99]. Additionally, Sn^{2+} has a strong tendency to oxidize to Sn^{4+}, driving rapid material degradation and compromising long-term stability. Sn^{4+} states at the surface form deep electron traps that contribute to non-radiative recombination [100]. To improve carrier extraction, both device architecture optimization and control of the initial doping level are crucial. To this end, a comprehensive understanding of defect formation, energetics, and their impact on optoelectronic properties is essential for enabling precise defect engineering strategies that balance charge transport and stability.

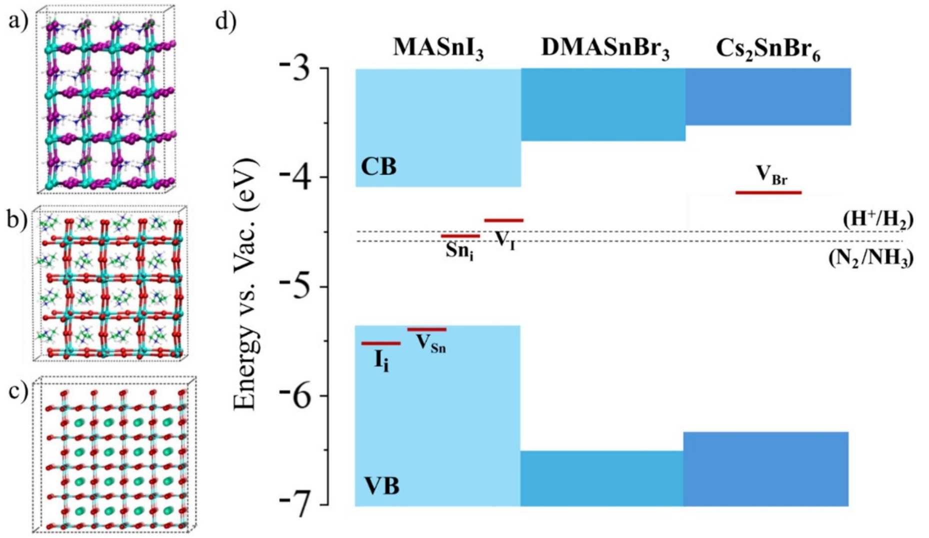

Figure 6. Crystal structure of (a) $MASnI_3$, (b) $DMASnBr_3$ and (c) Cs_2SnBr_6. The colour of the atoms are cyan: Sn, purple: I, red: Br, blue: N, green: C, white: H and turquoise: Cs. (d) Band alignment of $MASnI_3$, $DMASnBr_3$ and Cs_2SnBr_6 with respect to N_2/NH_3 and H^+/H_2 redox levels. The diagram also shows the thermodynamic transition levels for the halide vacancy, halide interstitial, Sn vacancy and Sn interstitial defects. All the values are referred to the vacuum level.

For PC, defects are not necessarily detrimental; rather, they can be designed to serve as active sites for catalytic reactions. In this context, the challenge is to position defects strategically to promote charge separation and reaction kinetics without introducing excessive recombination centres. The band positions and defect states must be carefully tuned to align with the redox potentials of the targeted reactions (figure 6(d)). Achieving this level of control requires not only precise material synthesis but also advanced characterization techniques to probe defect-related electronic states and their catalytic role.

Beyond defect engineering, another major challenge for both PV and PC is scalability. Current thin-film fabrication methods for PV rely heavily on toxic solvents and non-scalable techniques such as spin coating, posing environmental and industrial limitations. In PC, upscaling is further hindered by the difficulty of achieving uniform illumination in large-scale reactors. A promising alternative is to transition from conventional PCs to PEC systems, where oxidation and reduction reactions occur at separate (photo)electrodes connected through an external circuit. This approach allows for better light management, improved charge separation, and the ability to tailor each electrode specifically for its respective half-reaction. However, this shift necessitates the development of robust (photo)electrodes with optimized interfaces and long-term stability.

Advances in science and technology to meet challenges

To address the challenges associated with defects in THPs, various strategies have been explored to optimize material performance for both PV and PC. In PV, one of the most effective approaches to mitigate self-p-doping has been the use of additives like SnF_2 or dopants such as trivalent cations [101–103]. These strategies shift the Fermi level upward, destabilizing Sn vacancies by increasing their formation energy, thereby reducing their contribution to unintentional doping. Another key strategy involves optimizing processing conditions to prevent Sn oxidation, such as eliminating solvents like DMSO [104], which can facilitate the formation of Sn^{4+} species. Partial substitution of iodide with bromide has also been shown to be an alternative route to control charge carrier concentration, by simultaneously widening the bandgap and de-doping the material [105]. Beyond material design, advances in characterization techniques have played a crucial role in probing defects in THP. A significant challenge lies in distinguishing the effects of self-doping from deep traps, as their recombination timescales often overlap. Recent developments in advanced microscopy and spectroscopy, such as TAS across different spectral and temporal ranges and terahertz spectroscopy, coupled with simulations of charge carrier dynamics and DFT modelling, have enabled the differentiation of sub-bandgap and band-edge transitions [98, 106–108]. These techniques provide deeper insight into bulk and surface-related defect mechanisms, allowing for more precise defect engineering.

In PC, defect control must be approached differently. While avoiding self-electron trapping is crucial to minimize non-radiative recombination and ensure efficient charge separation, increasing the density of active site defects is essential to enhance catalytic activity. As an example, recent studies have shown that bromide vacancies in Cs_2SnBr_6 align well with the N_2/NH_3 redox level, potentially serving as active sites for ammonia production [93]. Similarly, filling oxygen into iodine vacancies in $DMASnI_3$ has been found to induce band shifts that improve alignment with CO_2 reduction redox levels [87]. As in the case of THP, surface defects play a constructive role in promoting catalytic activity also in other lead-free perovskite systems, like double perovskites. For instance, Bi-related defects have been found to enhance photocatalytic H_2 evolution [109], while CO_2 reduction has been shown to proceed more favourably on $Cs_2AgBiBr_6$ surfaces containing bromine vacancies [110]. These findings highlight the importance of defect positioning and chemistry in determining catalytic performance. Notably, despite the WBG of these materials, photocatalytic efficiencies have been tested under simulated sunlight conditions to better reflect real-world applications.

From a processing perspective, scalable and environmentally friendly deposition methods are critical for commercial viability. Efforts to replace toxic solvents with greener alternatives, such as isopropanol and GVL [111, 112], to be used in solution processed scalable techniques, like slot-die coating and printing techniques [113], and develop vacuum-free solution processing techniques will facilitate large-scale adoption. Additionally, real-time characterization methods are proving invaluable in correlating material properties with functional performance. These approaches enable a more comprehensive understanding of charge dynamics and defect behaviour, paving the way for rational material design in both PV and PC applications.

Concluding remarks

THPs hold immense promise for both PV and PC applications due to their tuneable structural and compositional properties, which directly influence their optoelectronic behaviour. Their versatility and unique defect chemistry allow for tailored designs suited to specific functionalities. While defects in THPs are detrimental to PV performance by introducing non-radiative recombination pathways, they can act as beneficial active sites in PC, underscoring the need for precise defect control strategies.

To fully harness the potential of THPs, key challenges such as defect engineering and scalable fabrication methods must be addressed. Continued advancements in material synthesis and advanced spectroscopic characterization will be essential for overcoming these limitations. With further research and optimization, THPs have the potential to bridge the gap between high-efficiency solar cells and effective photocatalytic systems, contributing to the development of sustainable energy technologies.

Acknowledgments

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5. Bismuth and antimony-based perovskites and derivatives

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Status

The emergence of LHPs set a new benchmark in materials for optoelectronics. However, the scientific community soon learned that their outstanding performance and ease of processability was in part offset their high environmental instability to moisture and heat. Likewise, the use of lead immediately triggered concerns of toxicity for their deployment within future products. These considerations were central in the push to find alternative materials within the 'perovskite family' with comparable optoelectronic properties, but with lower toxicity and improved environmental stability.

Initial work focused on tin- and germanium- based perovskites soon expanded into pnictogen elements (Bi and Sb) as lead replacements [114, 115]. Bismuth and antimony are suitable substitutes for lead, having a similar ns^2 configuration (when in +3 state), high polarizability, and far lower toxicity. Bi and Sb ions in their 3+ oxidation state cannot be directly substituted in place of Pb^{2+} and thus are unable to form a conventional ABX_3 perovskite structure. Instead, they form a *double perovskite* of the general formula $A_2B'B''X_6$ [116]. Here, A and X remain as monovalent cations and halide anions, but two divalent B cations in the conventional perovskite structure are replaced by a monovalent B′ cation and a trivalent B″ cation (Bi^{3+}, Sb^{3+}). Typical examples include $Cs_2AgBiBr_6$, $Cs_2NaBiCl_6$, $Cs_2AgSbCl_6$. Another class of materials featuring Sb and Bi is $A_3B_2X_9$ materials, that can be described as a *defect(vacancy)-ordered perovskite* [117]. These compounds can crystallize in either 0D or 2D forms wherein common examples include $Cs_3Bi_2I_9$, $Cs_3Sb_2I_9$ and $MA_3Bi_2I_9$. Finally, it has (for better or worse) become common practice to include in this list '*perovskite-like*' or '*perovskite-inspired*' materials, that do not technically adopt a perovskite (or pseudo-perovskite) crystal structure but are based on metal halides. Starting from the simplest BiI_3, relevant compounds in this category include silver bismuth iodides ($Ag_xBi_yI_z$) and analogous copper bismuth iodides [118], Sb(V) compounds (e.g. $CsSbI_6$) [119], and chalcohalides, with key compounds being BiOI, BiSI, BiSBr, SbSI [120].

Bismuth and antimony perovskites and derivatives offer favourable and tunable optoelectronic properties, and in many cases improved environmental stabilities over LHPs, making them suitable for many applications. We are just now digging below the surface of what is possible within this class of materials. Ongoing research to optimize their composition, stability, and performance is required to demonstrate their full potential.

Current and future challenges

Exploration of the expansive fields of double perovskites, vacancy ordered perovskites, and derivatives, has already yielded some promising avenues. However, they have yet to deliver on providing the desired environmental and chemical stability needed to compensate for their inferior semiconductor performance when contrasted against LHPs. Here, we outline the most important challenge areas to move the field forward as (i) Materials Discovery; (ii) Defect Chemistry, (iii) Morphology, Dimensionality, and Orientation. Advances in these areas all feed into the primary goal of improved stability and performance as outlined in figure 7.

The first challenge we identify relates to the (currently) inferior optoelectronic properties common to Bi- and Sb-based perovskite materials compared to LHPs. Many of these compounds have wide or indirect band gaps, large exciton binding energies (typically >100 meV) and subsequent short exciton diffusion lengths, which hinder efficient charge separation [121]. Their large hole and electron effective masses impact band-to-band transitions, both lowering their ground state oscillator strength and reducing carrier mobility. Strong carrier-structure coupling in their quasi-0D (vacancy-ordered) analogues localize excitons within a few unit cells. Moreover, strong electron-phonon coupling (to acoustic phonons) leads to charge carrier trapping (self-trapped excitons), limiting device performance. Fortunately, many of the aforementioned properties can be modified by compositional engineering, in the form of both tailoring existing compounds and uncovering new ones. As such, ongoing 'materials discovery' remains crucial.

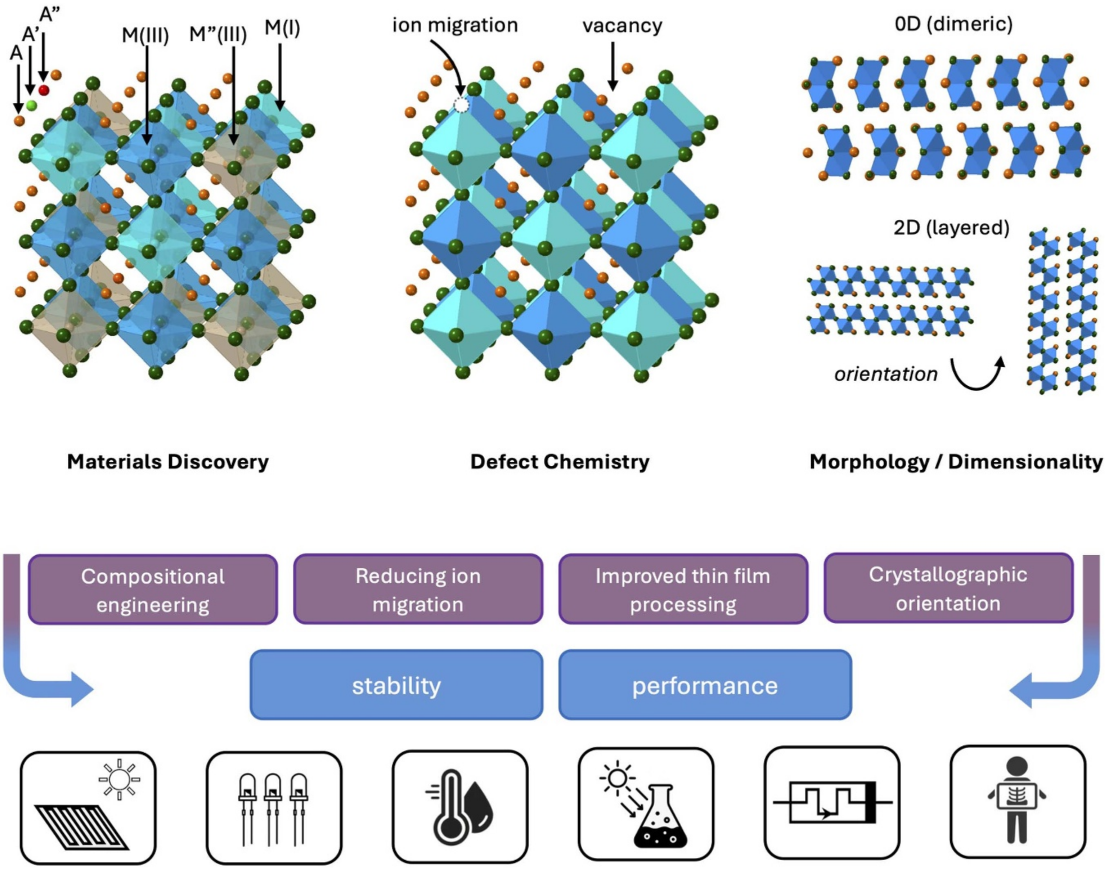

Figure 7. Summary of the main fields of advancement for bismuth and antimony perovskites and their derivatives. The road to applications with improved performances and stabilities spans a range of research areas including materials discovery and compositional engineering to enhance carrier lifetimes and improve band structure; achieving more stable lattice formations via reducing ion migration; employing compositional and chemical techniques to solve crystal defects; and make further progress in (thin film) morphology by controlling crystal dimensionality and harnessing orientation effects.

Discovery aided by ML and computational methods can provide valuable *a priori* data on material properties. Given Bi- and Sb-based perovskite materials include large, diverse, and complex classes of compounds, this data is indispensable to narrow the parameter space of potential candidates and guide experimental research. Only a subset of the materials combinations identified by computational evaluation as viable (thermodynamically stable with respect to tolerance factors) have been synthesized. More in depth computations can provide fundamental optoelectronic properties such as bandgap, density of states, absorption coefficient, expected carrier concentration etc and contrast these against thermodynamic structural stability. However, ML struggles to provide guidelines on other aspects such as environmental stability (decomposition or phase transition when subject to external factors including temperature, oxygen, moisture) and defect tolerance. This is exacerbated by the complexity of compositions and structures of these materials, which makes both computational simulations, and accurate ML predictions very challenging, especially with small training sets [122].

Another critical challenge we identify is morphology. Irrespective of the material properties, an appropriate thin film morphology is a critical factor for the successful integration of novel materials into devices to avoid charge recombination at interfaces and GBs, which severely impact device efficiency and stability. Vacuum-based (evaporative) depositions are excellent at generating coatings with controlled morphology. However, the complexity of multi cation and anion systems typical of Bi/Sb perovskites makes these methods less practical–especially when organic cations are required. On the other hand, solution-based methods are appealing for both material discovery and device fabrication. However, materials produced by wet chemical methods more readily suffer from poor film quality, including pinholes (coverage issues), inadequate grain formation, and phase segregation. A key challenge is the difficulty to match solubilities of the (multiple) precursors and obtain phase pure films even before morphological improvements can be made. The poor solubility of many M(I) and M(III) chlorides and bromides, and the corresponding hard cations like Cs and Rb in commonly employed solvents like DMF, DMSO, γ-Butyrolactone (GBL), and NMP is difficult to overcome.

Research efforts on Bi/Sb perovskites have recently expanded to achieve control over crystal dimensionality (0D, 2D, etc) and crystallographic orientation [25]. Given the low dimensionality common to these perovskite compounds, control over orientation is essential to optimize charge transport. However, this adds another layer of complexity during film fabrication and requires knowledge of how to practically manipulate the formation and surface energies of opposing crystal facets. At present there is no general strategy to handle this, and advancements must be made empirically.

Beyond tackling the challenges of film morphology and material limitations, the development of efficient and stable Bi/Sb perovskite materials remains a major hurdle due to their excess defects, including point defects and lattice defects, which negatively impact optoelectronic performance. The trap density observed in bismuth- and antimony-based perovskites can be 2–3 orders of magnitude higher than that of LHPs ($\sim 10^{17}$–10^{18} cm^{-3},compared to $\sim 10^{15}$ cm^{-3}) [123]. This significantly increases non-radiative recombination, limiting carrier diffusion lengths, which have been measured to be as short as ∼60–140 nm in $Cs_3Bi_2I_9$—well below commonly observed diffusion lengths for LHPs (>100 μm) [124]. Addressing these defects is crucial to reducing Urbach energy losses and V_{OC} deficits for PV devices [8]. It is important to state that all these considerations are relevant to (opto)electronic devices, while some surface defects might indeed be desirable for applications in (photo)catalysis, because they can provide sub-bandgap optical absorption, and preferential sites for molecules adsorption and decomposition [125].

Finally, although the phenomenon of ion migration is well established across perovskite materials, even for LHPs the mechanisms are not yet fully understood. This becomes increasingly complex for Bi/Sb perovskite derivatives as multiple ions can migrate via different pathways [126]. More studies are needed on formation energies of some of these ionic species, and their diffusion energy barriers. Understanding how these ions behave within the lattice under light and heat is pivotal to unravel (possible) degradation pathways to improve material stability and device durability.

Advances in science and technology to meet challenges

The exploration of perovskite derivatives remains in its early stages. Despite research work spanning back around a decade vast compositional possibilities are still yet to be realized. A synergistic approach that combines experimental synthesis with theoretical modelling and AI-assisted ML prediction will accelerate the discovery of novel materials with optimized properties. It is fundamental that appropriate, comprehensive training sets are developed for the ML algorithm, and data sharing and collaboration across the research community will be vital in achieving this goal [127].

Compositional engineering will be critical to stabilizing target compounds, mitigating carrier-trapping effects, improving charge mobility, and enhancing efficiency. Hybridization at the M(III) site, and multi-cation hybrids allow fine-tuning of the optical properties, offering new pathways to tailor absorption and emission characteristics [116]. Additionally, the introduction of lanthanides at the M(III) site presents a promising strategy for achieving the necessary radius ratio to stabilize iodide-based double perovskites [128]. Structural stability can also be improved through strategic A-site modifications, incorporating double or triple cation systems to help compensate for any inherent (or introduced) lattice instabilities [129]. While some of these materials are more stable than LHP, studies on their long-term stability are lacking and should be regularly incorporated into ongoing research.

Future advancements in bismuth and antimony perovskites will undoubtedly rely on improving material morphology and optimizing charge transport. Many detrimental attributes, including extensive GBs (small grain sizes), interface irregularities, and pinholes, can be mitigated through relatively simple solvent engineering (*i.e.* using hybrid solvents with tailored vapour pressures and coordination strengths), film formation strategies such as hot casting, as well as post treatments, including rapid vacuum annealing and solvent (or metal halide) vapour annealing [130]. An effective strategy to overcome precursor solubility issues is to use aqueous (acid-based) systems to first synthesize and purify the desired compound as a bulk powder, which often has a far higher solubility that its individual counterparts. Another approach involves using additives that aid solubility and facilitate thin film formation but do not become part of the final thin film [131]. These transient agents decompose or evaporate, leaving behind a pristine material and even have the possibility to control crystallographic orientation. Morphological issues should also be tackled through advances in deposition techniques, for example through confined space growth, inverse temperature crystallization, and spray coating [132]. In addition, the use of pre-formed perovskite nanocrystals as building blocks can offer new avenues for film deposition with controlled morphology, including high surface area for applications in catalysis [133].

Importantly, as the field progresses, researchers should consider toxicity aspects of the fabrication process. DMF poses serious health hazards, and its use has already been heavily restricted in many countries, with similar concerns being raised for NMP. Greener alternatives such as GVL, cyrene and ionic liquids should be further explored [134].

Another crucial challenge is transforming 0D materials within this class into 2D layered structures to enhance charge transport. Additional benefits can then be realized through appropriate crystal orientation (with respect to the electrodes). Early work in the field demonstrated that chlorine-based additives can facilitate the 0D-2D conversion in Sb-based vacancy ordered perovskites, showcasing a potential route to improved optoelectronic performance [135]. Furthermore, layered structures offer distinct advantages, including naturally passivated GBs (without dangling bonds), which can reduce non-radiative recombination, ultimately leading to higher efficiency in optoelectronic devices [136]. Further advancements rely on continuing targeted investigations into using larger or more exotic organic ligands at the B-site, anion exchange strategies, ligand-mediated facet growth, and thin film fabrication protocols to uncover new processes that can modify crystal dimensionality and orientation. The future success of bismuth and antimony perovskites also hinges on a deeper understanding and mitigation of defect-related challenges, starting with the systematic investigation of defect nature and energetics. Differentiating between shallow and deep traps, mapping their density distribution as a function of composition, and quantifying their formation energies will provide a foundation for effective trap reduction strategies. By integrating theoretical modelling with advanced experimental techniques, researchers can develop a more comprehensive understanding of defect behaviour and their influence on device performance. Notably, some pnitctogen-based perovskites maintain low non-radiative recombination rates despite high defect densities, potentially due to their defect energy levels being within ~100 meV of the band edges or possessing low capture cross-sections. Investigating whether defect tolerance in these materials arises from shallow defect states, or self-healing mechanisms will provide much needed insights. It is expected that enhancing material properties through compositional tuning will be central to mitigating defects. Employing high-polarization cations, particularly through strategic mixing of M(III) cations, can increase the dielectric constant of the material, effectively reducing capture cross-sections (trapping) thus minimizing the influence of defects. Additionally, surface treatments with specific elements can passivate dangling bonds, further improving optoelectronic properties and stability [137]. To accelerate progress, we believe the field should also prioritize studies on single crystals, as they offer a cleaner platform to isolate the most promising compositions and address the cause and impact of defects without the complexities introduced by GBs and polycrystallinity [138].

Concluding remarks

Pnictogen-based perovskite and perovskite-inspired materials still have untapped potential to be key contenders in optoelectronics, sensors, and catalysis. Some of these compounds with suitable optoelectronic properties have already been proven to be highly effective for selected applications, including IPVs, x-ray detection, and PCs. In applications such as solar PVs, LEDs and photodetectors, they are still well behind the benchmarks set by LHP.

To systematically address the challenges outlined above diligent research should primarily be focused in the areas of compositional engineering, increasing crystal dimensionality (and orientation), defect chemistry, and thin film morphology. Advancements in any one of these key areas will elevate the performance of bismuth and antimony perovskites and expand their application base to achieve devices with improved stability and durability.

Looking ahead beyond traditional double perovskites and derivatives we believe the field must expand its scope to include underexplored classes of materials. These may include bismuth and antimony *chalcohalides* to provide some of the materials processing advantages of metal halides while retaining the stability common to metal chalcogenides [139]. Likewise, electronically reverse perovskites, termed *anti-perovskites* are emerging materials, which preserve a similar perovskite structure with the advantages of accommodating a wider varieties of elements [140]. Continued advancements in line with the initial motivation—to find better bismuth and antimony perovskites and derivatives to compete with LHPs—will establish the next generation of high-performance semiconductors.

Acknowledgments

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6. Copper-based perovskite derivatives

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Status

Copper exists in either a +1 or +2 valence state in halide- and chalcogenide-based CPDs. In the +2 state, copper in octahedral coordination typically forms 3D or 2D crystal structures. In the +1 state, copper binds with halide or chalcogenide ions in tetrahedral or triangular planar coordination, leading to 1D or 0D structures. CPDs has been studied for various light-harvesting applications and a recent study of the authors highlighted the promising potential of a Cu(I) iodide containing CPD for sustainable IPVs [141].

2D layered organic-inorganic compounds, $(CH_3NH_3)_2CuCl_4$ and $(CH_3NH_3)_2CuCl_2I_2$, were among the first Cu(II) halide CPDs tested for solar cells, with the highest PCE of 2.41% (figure 8(a)) [142]. On the other hand, Cu(I)-based CPDs like $CuBiI_4$ and Cu_2AgBiI_6 show excellent phase- and photo-stabilities [143]. Copper pnictogen halides achieved a maximum solar cell PCE of 1.1% [144]. Cu_2AgBiI_6, which has a high absorption coefficient (10^5 cm^{-1}) [145], demonstrated solar cell PCE of 1.8%–2.4% through material and device engineering [118, 145, 146]. A PCE of less than 10% has been achieved for Cu_2AgBiI_6 with the Sb incorporation under indoor light intensity [146]. Cu_2AgBiI_6, with its WBG of 2.0 eV, can potentially achieve 30% PCE in single-junction IPVs and 30.2% PCE as a top cell in Si-based tandem solar cells [28, 145]. This emphasizes the development of WBG CPDs for low-cost and low-toxicity PVs.

Cu(I)-based chalcogenide CPDs, with the general formula $CuBCh_2$,where B = Sb or Bi and Ch = S or Se, exhibit direct bandgaps of 1.0–1.6 eV, making them suitable for solar light harvesting [150]. Although Bi-based chalcogenide compounds have been studied for solar cell applications [151], Sb-based compounds, particularly $CuSbSe_2$, remain the most promising $CuBCh_2$ absorber material. $CuSbSe_2$, with negligible cation disorder and band-like transport, processed through a vacuum-based approach, has achieved a solar cell PCE of 4.7% using a CdS charge transport layer [152]. Recently, solution processing of $CuSbSe_2$ in a thiol-amine medium has been reported [149].

CPDs, especially halide-based ones have shown a great promise for photo(electro)catalysis including CO_2 and CO reduction, and PEC water splitting (H_2/O_2 generation) because of tunable bandgaps, high absorption coefficients, and environmentally friendly characteristics. Hybrid CPDs ($Cs_3Cu_2I_5$@ZIF) [153] and heterojunction ($CsCuCl_3$/Cu [147] and Cs_2CuBr_4/CeO_2 [154])-based photocatalysts have improved selectivity and efficiency of CO_2 reduction (figure 8(b)).

Thus, despite their early-stage application, CPDs possess a great potential for both PCs and a wide-range of PV applications.

Current and future challenges

CPDs have underperformed in PV efficiency for both outdoor and indoor applications, falling significantly short of LHPs, indicating substantial room for improvement. Stable and WBG Cu(I) halide CPDs are highly promising for IPVs and tandem solar cells, with theoretical PCEs of ~30%. However, strong carrier localization in this material, which is commonly observed in other low-dimensional perovskite derivatives, hinders efficient charge carrier extraction. Combined with unoptimized thin film morphologies featuring small grains and large pinholes, this ultrafast carrier localization, due to low electronic dimensionality, contributes to short-circuit current (I_{SC}) and V_{OC} losses [155]. Thus, it is urgent to get insights into how charge carrier localization may be avoided in these materials.

One alternative strategy is to develop 3D copper halide elpasolites, although 3D structural dimensionality does not necessarily guarantee 3D electronic dimensionality. 3D halide elpasolites, like $Cs_2CuBiBr_6$, $Cs_2CuSbBr_6$, and $(CH_3NH_3)_2CuInCl_6$, with direct and tunable bandgaps, have been predicted [156]. But, experimentally realizing such 3D CPDs with 3D-connected $[CuX_6]$ octahedra is rare due to the tendency of Cu(I) to favour 3- or 4-fold coordination. Conversely, layered $Cs_4CuM_2Cl_{12}$ (M = Sb and In), which feature $[CuCl_6]^{4-}$ octahedra sandwiched between two layers of $[MCl_6]^{4-}$ octahedra, are experimentally reported (figure 8(c)) [148, 157]. Highly stable $Cs_4CuSb_2Cl_{12}$, with a direct bandgap of 1.0 eV and a dispersive electronic band structure (figure 8(c)), exhibits low effective masses

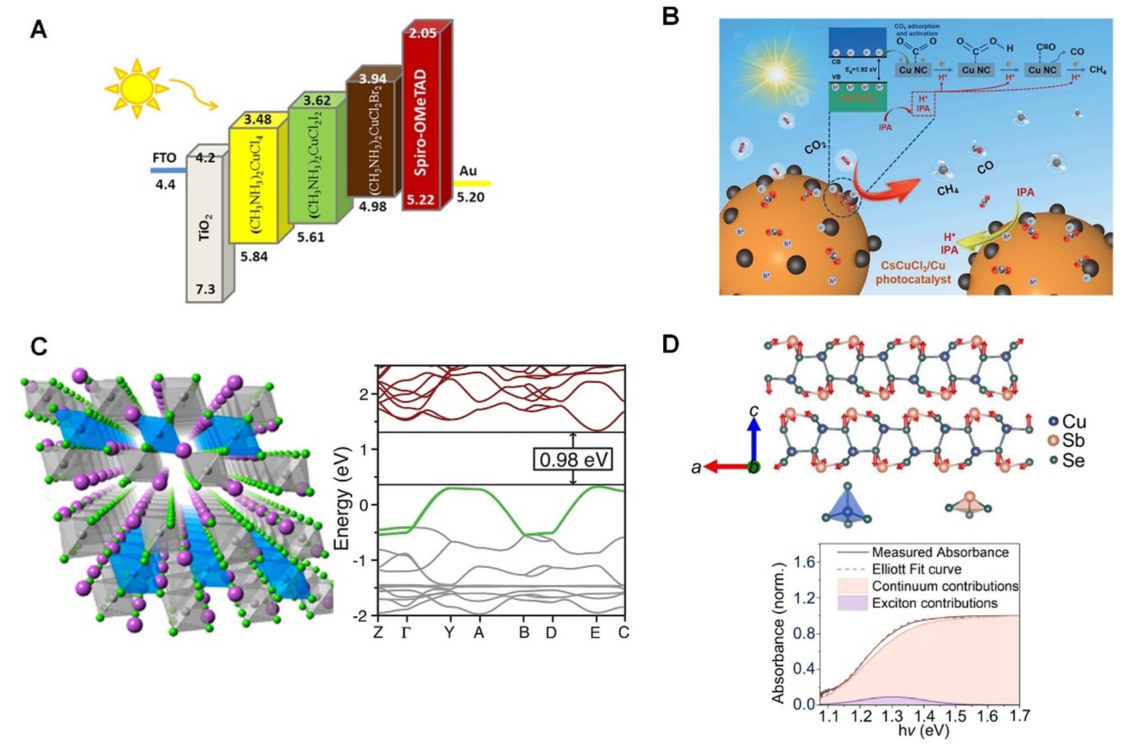

Figure 8. (A) Photovoltaic device architecture and energy level alignment of the $(CH_3NH_3)_2CuX$. Reprinted with permission from [142]. Copyright (2018) American Chemical Society. (B) Photocatalytic CO_2 reduction reaction using $CsCuCl_3$/Cu heterojunction. [147] John Wiley & Sons. © 2023 Wiley-VCH GmbH. (C) Left panel: Crystal structure of $Cs_4CuSb_2Cl_{12}$ [148]. Cl and Cs atoms are depicted as green and purple spheres, respectively; Sb and Cu coordination polyhedra are shown in gray and blue, respectively. Right panel: DFT-calculated band structure of $Cs_4CuSb_2Cl_{12}$ (Energy *versus* high-symmetry points) [148]. Occupied, partially occupied and unoccupied bands are displayed in gray, green and red, respectively. Reprinted with permission from [148]. Copyright (2017) American Chemical Society. D. Top panel: Crystal structure of $CuSbSe_2$ (shown along the *b* axis). Bottom panel: Comparison between the measured optical absorbance curve and its Elliott model fit for revealing the exciton binding energy of ∼9 meV. Reproduced from [149].

for holes (0.16 m_h) and electrons (0.32 m_e), comparable to $CH_3NH_3PbI_3$, making it an excellent candidate for solar-to-electricity conversion [148]. Surprisingly, the use of $Cs_4CuSb_2Cl_{12}$ or other $Cs_4CuM_2Cl_{12}$ in PVs remains almost unexplored, likely due to the challenges in processing these CPDs into high-quality thin films.

While carrier localization and cation disorder contribute to large Urbach energies and PV device performance losses in halide CPDs, chalcogenide CPDs, particularly $CuSbSe_2$, are not expected to suffer from these issues [149]. This results in improved carrier mobilities for $CuSbSe_2$. However, achieving high-quality thin film morphologies through solution processing and determining the optimal device architecture remain challenges for both halide and chalcogenide CPDs.

The challenges for using halide CPDs in PCs include structural instability, sensitivity to environmental factors, insufficient active sites, inefficient charge carrier utilization, slow reaction rates, and poor performance as photocatalysts for CO_2 reduction and other reactions. Further research, combining experimental and theoretical calculations, is needed to investigate excitonic delocalization, localization, and self-trapping in CPDs. This will enrich the photophysical dynamics and improve the performance of CPDs based photocatalysts.

Advances in science and technology to meet challenges

To fully harness the potential of CPDs for PVs, it is crucial to focus on controlled film processing strategies that achieve superior microstructure with maximized grain sizes, minimized pinholes, and reduced bulk and surface defects. A key challenge in achieving high PV efficiencies in halide CPDs is ultrafast carrier localization, which intensifies as electronic dimensionality decreases. For instance, despite the 2D structural dimensionality of Cu_2AgBiI_6, its electronic dimensionality is much lower. Conversely, $CuSbSe_2$, with its near-2D crystal structure, exhibits nearly 3D electronic dimensionality due to Sb-Se anti-bonding states at the conduction band minimum and quasi bond formation at the interlayers, ensuring band-like transport, and low exciton binding energy of ∼9 meV (figure 8(d)) [149].

Understanding the crystal structures of CPDs and their relationship to optical, electronic, and ionic properties is essential. This knowledge will help identify CPD absorbers with desired optoelectronic properties for light-harvesting and develop design principles for new CPD absorbers with band-like transport and low exciton binding energies.

Despite the inherent defect tolerance and band-like charge transport in $CuSbSe_2$, solar cell efficiencies have stagnated at less than 5%, mainly due to huge V_{OC} losses ($\sim$0.70 V V_{OC} deficit relative to the radiative limit) [152]. Emerging consensus from simulations and initial proof-of-concept device stacks suggests that the bottleneck lies not in bulk transport but in misaligned and defect-rich interfaces. The conventional CdS creates a detrimental conduction band cliff of ≈–0.43 eV, which accelerates interfacial recombination. Substituting CdS with composition-tunable $Cd_{1-x}Zn_xS$ enables adjustment of the conduction band offset, shifting it towards a small positive spike of around +0.05 eV [158]. Numerical optimization suggests that retuning the Zn content (x) or the O/S ratio in Zn(O,S) could increase simulated efficiencies to $\sim$8–10%, with V_{OC} approaching 0.443 V [158]. Experimentally, Cd-free ZnSnO window layers have already boosted solar cell efficiency from 2.1% to 2.4% [159]. On the p-type side, introducing a thin, highly doped p^+ back-surface-field (Cu_2O, MoS_2 or $CuGaSe_2$) on top of the Mo/$MoSe_2$ back contact can suppress the rear barrier [160]. Complementary post-deposition treatments with alkali fluorides (NaF, KF) and front-side passivation using a very thin Al_2O_3 or benzoic acid self-assembled monolayers can jointly cut interface recombination [161]. Additionally, Cu-poor/Sb-rich co-evaporation at 350 °C consistently yields $\sim$2 μm grains [162], indicating that bulk $CuSbSe_2$ is ready for >10% efficiency devices once interfacial losses are fully addressed.

A concise comparison with the benchmark chalcopyrite system $CuInSe_2$/Cu(In,Ga)Se_2 (CIGS) helps contextualize the potential of $CuSbSe_2$. After five decades of materials optimization, band gap grading, and alkali activation, CIGS now achieves >20% laboratory PCE with a V_{OC} deficit of only <0.40 V [163]. In contrast, current $CuSbSe_2$ devices reach just 4.7% efficiency, with losses attributed primarily to interface recombination rather than bulk limitations like strong carrier localization [149]. Crucially, $CuSbSe_2$ shares CIGS's strong optical absorption but is free of indium and gallium, and crystallizes $\sim$200 °C [164], making it compatible with lightweight substrates and less susceptible to supply constraints. Closing even half of the current V_{OC} gap—via ETL engineering, back surface field enhancement, and alkali/passivation strategies (as discussed above)—could elevate $CuSbSe_2$ beyond the 10%–15% efficiency threshold, positioning it as a viable indium-free contender in thin-film PVs.

Therefore, device engineering is crucial, focusing on identifying or designing suitable charge transport layers that minimize band alignment mismatch, accelerate carrier transport, and form less-defective interfaces to reduce PV parameter losses in both halide and chalcogenide CPDs. Additionally, computational techniques like DFT calculations, ML, and design of experiments play a crucial role in predicting the structure, stability, optoelectronic properties, and optimal device layers and configurations of targeted CPDs, minimizing experimental trial-and-error.

Current challenges of halide CDPs for PCs include inferior efficiency, poor stability, and unclear reaction pathways. Strategies to overcome these include: (1) enhancing active sites on photocatalysts boosts adsorption and redox reactions. Understanding CPD structures and altering their morphology improves performance. Adding surface additives or supporting agents for increased active sites. (2) Incorporating suitable elements or creating heterojunctions can optimize performance by ensuring the bandgap match or exceed the light source, leading to efficient light absorption and faster reactions. (3) A unified evaluation method is necessary to address significant issues in CPDs-based photocatalysts. Additionally, a comprehensive theoretical model is required to explain their high catalytic activity. (4) Addressing the structural and chemical stability of CPDs is essential for long-term activity. (5) Using advanced AI techniques like deep learning and ML can help model materials and predict the optimal composition for CPD photocatalysts.

Beyond bulk thin films, CPDs are now being engineered in quantum-confined and topologically non-trivial architectures that open fresh avenues for light-energy conversion. Colloidal $Cs_3Cu_2I_5$ and Cs_2CuBr_4 quantum dots already show ⩾30% photoluminescence quantum yield [165] and enhance the CO_2-to-fuel selectivity compared to their bulk analogues, highlighting their promise as spectrum shifters or catalytic absorbers [147, 153, 154]. At the other extreme of dimensionality, chain-like layered double perovskite $Cs_4CuSb_2Cl_{12}$ combines a direct 1.0 eV bandgap with low carrier effective masses ($m_e \approx 0.32\ m_e$), marking it as a yet-untapped lead-free absorber for thin film PVs [148]. While first-principles studies confirm a direct bandgap with low carrier masses for $Cs_4CuSb_2Cl_{12}$ with corner-sharing CuX_6 framework, explicit predictions of Dirac or nodal-line states have so far been largely confined to oxide-based kagome networks [166], leaving the Cu-based halide and chalcogenide families unexplored and intellectually open for future theory–experiment investigations.

Concluding remarks

CPDs show great promise for light-harvesting applications like PVs and PCs due to their low-toxicity elements (including copper itself), high structural stability, direct and tunable bandgaps, and high absorption coefficients. WBG halide CPDs are particularly attractive for IPVs and tandem solar cells, while chalcogenide derivatives like $CuSbSe_2$ are promising for efficient solar light harvesting due to their narrow bandgaps. However, the current performance of CPDs in both PVs and PCs is subpar due to low electronic dimensionalities, high exciton binding energies, strong carrier localization, and limited understanding of structural-property relationships. The lack of optimized device architectures further exacerbates these performance issues. Recent studies on $CuSbSe_2$ highlight the importance of understanding the fundamental correlations between crystal structure and electronic properties to identify and design near-ideal PV absorbers and photocatalysts based on CPDs that possess low exciton binding energies and high electronic dimensionalities for ensured band-like carrier transport. Additionally, employing advanced theory models and AI predictions will accelerate the design of efficient CPD light-harvesting devices.

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7. Advanced characterization of emerging lead-free solar absorbers

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Status

In the search for environmentally-friendly alternatives to LHPs, a novel family of lead-free, metal halide solar absorbers based on non-toxic metal cations, such as Cu(I), Ag(I), In(III), Bi(III), and Sb(III) cations has recently emerged. Together with inorganic absorbers that include chalcogen anions (e.g. Bi(III), Sb(III) chalcohalides and ABZ_2 chalcogenides), this class of materials is often referred to as PIMs [114]. PIMs have garnered increasing attention as solar absorbers, owing to the reported high absorption coefficients ($>10^5$ cm^{-1}), relatively low electron and hole effective masses (down to $\sim 0.3\ m_0$), low-temperature processing, and reduced toxicity [114]. However, despite their potential in PV and photo(electro)catalytic applications, lead-free PIMs are still lagging behind the performance of lead-halide perovskites. PCEs for PIM-based solar cells are comparatively modest, with record efficiencies of 6.37% [37] and 10.8% reported for $Cs_2AgBiBr_6$ and $AgBiS_2$-based solar cells [167] respectively; well below the 26% efficiency reported for $FAPbI_3$-based PVs. The large disparity in the PCE of these devices reveals an urgent need to understand the factors which limit the performance of these materials.

Initially, fabrication challenges arising from the poor compatibility of standard perovskite processing methods with more complex PIM compositions were identified as primary barriers to PIM device performance [168]. However, more recently, fundamental questions regarding the photophysics and the related intrinsic performance limits of these lead-free materials have also come to the forefront of PIM research. Several of the most studied PIM compositions (such as Ag(I)Bi(III), Ag(I)Sb(III), Ag(I)In(III), Cu(I)Bi(III)-based) have reported WBGs (around 2 eV), non-negligible exciton binding energies (>100 meV) and low dimensionality (structural and electronic), potentially impairing device performance with respect to their lead-based counterparts [8]. Furthermore, recurrent broad emission linewidths and fast photoconductivity decay have raised concerns regarding the role of localized charge carriers [63, 169]. To elucidate the photophysics of PIMs, various advanced characterization techniques have been employed, ranging from transient absorption, photoconductivity and luminescence probes to photocurrent-based methods [8]. Overall, the studies indicate that poor charge-carrier transport and extraction in PIMs is a major limiting factor for their use as solar absorbers in solar cells [8, 115]. Therefore, further research is urgently needed to guide the rational development of PIM compositions, circumventing the generally observed intrinsic limitations. Combined with improved processing and new device architectures, this research direction promises to unlock the potential of this large class of lead-free solar absorbers.

Current and future challenges

Figure 9 schematically shows the roadmap for the characterization of emerging lead-free absorbers. Elucidating the main factors impairing charge-carrier transport in PIMs and unveiling structure-property relationships with which to navigate the vast compositional space available is the first and foremost challenge in the characterization of these materials. In the following, we identify significant open questions in this space:

Phonon coupling. Understanding intrinsic limits to charge-carrier transport in this class of materials is critical for the rational development of PIMs. Owing to the partially ionic nature of metal-halide bonds, phonon interactions are expected to be a major contributing factor to charge-carrier scattering rates in these materials. The initial reports of strong phonon coupling in double perovskites, such as $Cs_2AgBiBr_6$, together with the low reported charge-carrier mobility (1–4 $cm^2\ V^{-1}\ s^{-1}$ in thin films, in contrast to $\sim$30 $cm^2\ V^{-1}\ s^{-1}$ reported for lead-halide perovskites [115]) underscore the importance of elucidating these fundamental constraints. Furthermore, recent reports of ultrafast charge-carrier localization processes [169]—i.e. observed as ultrafast decay of the charge-carrier mobility—and their assignment to self-trapping processes [63] further compound the urgency of determining such phonon coupling

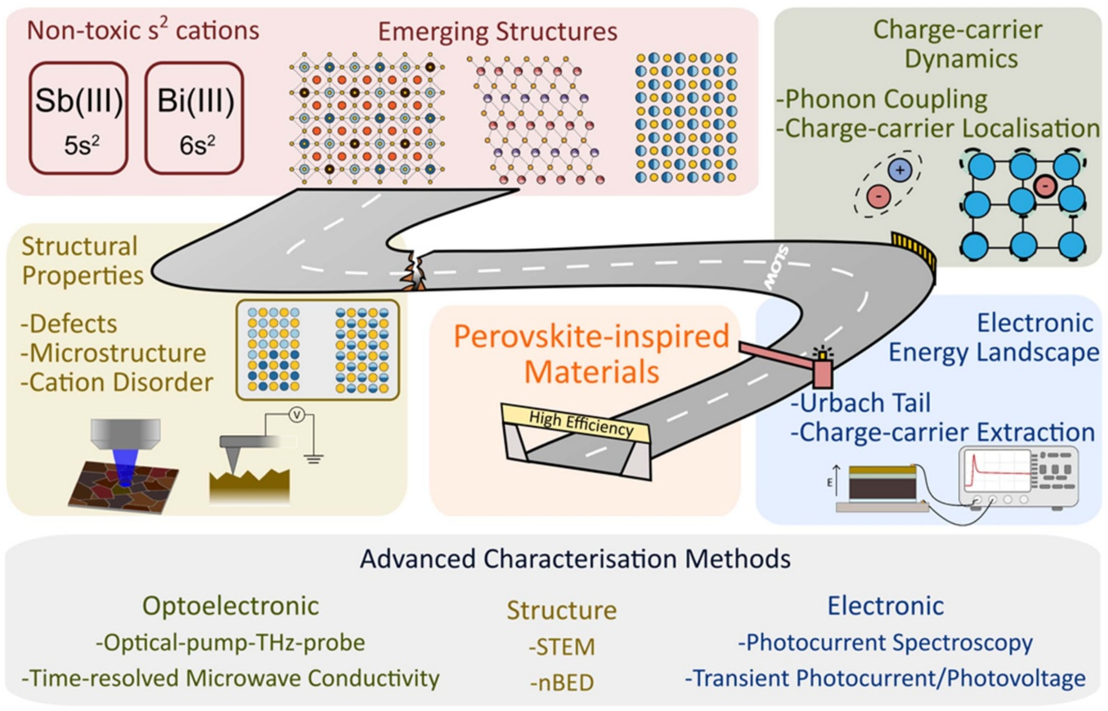

Figure 9. Schematic representation of the roadmap for emerging perovskite-inspired materials. Building on the wide compositional and structural space available, improved understanding of the structural properties, the charge-carrier dynamics and the electronic energy landscape are needed to enable higher efficiencies in solar energy conversion applications. In the bottom panel, are indicated optoelectronic, structure and electronic characterization methods for the advancement of PIMs (Acronyms: STEM—scanning transmission electron microscopy, nBED—nano-beam electron diffraction).

mechanisms. A particular challenge will be disentangling short-range phonon interactions (e.g. deformation potential interaction) from the usually-dominant Fröhlich coupling mechanism, where a range of temperature and pressure-dependent photoluminescence, Raman, and photoconductivity studies could prove useful. Such insight will relate to open questions regarding the 'softness' and anharmonic character of these semiconductors, which were opened by LHPs [170]. Overall, unveiling the nature of phonon-coupling mechanisms in PIMs will clarify intrinsic limitations for charge-carrier transport in these materials and, combined with first principles modelling, will enable the rational design of new compositions capable of transcending these limitations.

Defects and defect-tolerance. Mastering the physics and chemistry of defects in PIMs is urgently needed to mitigate extrinsic limits to charge-carrier transport in this class of materials. While PIMs' research has focused on ns^2 metal cations that are, in principle, capable of replicating the defect-tolerant properties of LHPs, deep traps have been identified as an important recombination channel both by DFT calculations and photoconductivity probes, in several lead-free perovskites, such as $Cs_2Ag(Bi,Sb)Br_6$, Cu_2AgBiI_6, $Cs_2AgInCl_6$, and perovskite-inspired compositions [8, 171], such as BiOI, $CuSbSe_2$, and $AgBiS_2$ [172, 173]. Crucially, elucidating the nature of defects in these materials and their impact on charge-carrier dynamics is a fundamental yet challenging task that requires a combined approach with multiple probes. Even though photoluminescence has been conventionally used to probe charge-carrier dynamics, the combination of weak band-to-band emission and intense emission from localized and defect states can be potentially misleading [169, 174]. Therefore, combining this with transient photoconductivity and photocurrent probes will be necessary to distinguish long-living mobile charge carriers from localized and trapped ones. Such insight will help narrow down the vast compositional space available, identifying the most promising and more defect-tolerant compositions to develop and optimize.

Advances in science and technology to meet challenges

Microstructure and transport. Beyond intrinsic phonon coupling and extrinsic defect recombination, the desired long-range charge carrier transport in these emerging semiconductors is also impaired by their microstructure [175]. Hence, further advances in PIM device efficiencies will no doubt be fuelled by an improved understanding and optimization of the extended microstructure of PIM thin films. Many PIMs of interest, like halide perovskites, are compound semiconductors where thin-films are deposited through simple solution-processing, or vapour deposition techniques. In the case of halide perovskites, one of the underlying causes of their unprecedently rapid performance increases is the significant improvement in the quality of thin-films. This has largely been achieved through the modulation of thin-film crystallization kinetics. In the case of solution processing, this has been done by careful control of precursor ink chemistry, for example, through the inclusion of small amounts of highly coordinating solvents such as DMSO or NMP, combined with improved processing techniques such as anti-solvent or gas quenching. By ensuring both high solubility of the precursor materials and rapid, burst, nucleation on the desired substrate; this approach has allowed for the development of high-quality, uniform and pinhole free films. A variety of precursor ink additives (such as large ammonium cations, Lewis bases, etc) have been included to induce intermediate phases, or as structure directing agents to control both orientation and size of the crystallites in the thin-films, further improving both optoelectronic properties and eventual device performance. While this exact additive-based approach is difficult to replicate in the case of vapour deposition, thin-film quality, optoelectronic properties and device performance has also been improved through the inclusion of additives such as $PbCl_2$ [176], or through using templating layers [177] to control the growth of thin-films. Taking inspiration from the plethora of work on halide perovskites, using approaches such as these, in a consistent feedback loop with probing the impact of microstructure on the optoelectronic properties of these PIMs will hasten their development.

Another crucial aspect of these multicomponent systems is the impact of nanoscale heterogeneity on bulk properties. The rising interest in more complex material compositions has created a multitude of approaches for tailoring the properties of PIMs solar absorbers. However, such increasing complexity also enhances the role played by defects and disorder. Owing to the similarity of metal cation radii used in PIMs, special attention should be dedicated to antisite defects, which have proven detrimental in kesterites. Crucially, however, a fine-tuning of the metal cation site occupancy in PIMs could be a game-changer for tuning the electronic and transport properties of these materials. For instance, Ag/Bi cation disorder in PIM has proven effective in narrowing the bandgap, increasing the absorption coefficient [178] and enhancing transport [173]. Despite these initial promising studies, significant advances in the characterization of these materials are urgently needed to observe and quantify cation disorder in PIMs. Here, heterogeneity in structure and composition often remains undetected in bulk measurements such as XRD, but often have significant impact on material stability. Probing atomic and nanoscale structure using high-resolution imaging and diffraction techniques such as STEM and nBED, combined with compositional data obtained through spectroscopic techniques such as EELS and EDX will provide valuable insight here. Coupling these multi-length scale chemical and structural characterization techniques with probes of charge-carrier dynamics, such as mobility, for example, will be critical in probing the differences between fundamental material properties and thin-film properties, allowing for effective material screening. In the cases where a particular promising material has been identified, efforts should then focus on improving film-quality from the atomic scale to the macroscale, before moving on to complex device processing.

Electronic energy landscape. Electric fields. Akin to early organic PV devices, charge-carrier localization and subsequent extraction have been the critical bottlenecks in realizing efficient PIM-based devices. Therefore, to develop a comprehensive understanding of the impact of broadened band tails and localized charge transport under an electric field, e.g. in device applications, a combination of electrical and spectroscopic techniques is essential to bridge the gap between material and device properties.

PCS, TPC and TPV are techniques that bridge this gap and have consistently been advanced to troubleshoot charge-carrier dynamics in thin-film heterojunction devices. By characterizing an electrical signal as a function of photon energy and/or time, PCS eliminates the scattering and reflection artifacts common in standard spectroscopic techniques. This results in exceptional dynamic range, enabling precise identification and location of defect states as well as detailed breakdown of charge-carrier generation, transport and extraction dynamics [179].

The Urbach tail represents an amalgamation of static and dynamic disorders within photoabsorbers, which are especially prominent in PIMs, and must be characterized with high precision, giving researchers a reliable reflection of PIM thin film quality in devices [180]. To verify the true impact of the charge-carrier dynamics observed in neat PIM thin films, applying a varying electric field in PIM devices during PCS and TPC measurements, will give insights into drift/diffusion-mediated charge-carrier transport and extraction processes. Moving beyond the steady state, utilizing *ultrafast* PCS in PIM-based devices will help elucidate the trapping and detrapping mechanisms of localized charges in the presence of an electric field [181]. Evaluating the limiting mechanisms of PIMs in the context of device operation will provide guidelines for developing novel device concepts (e.g. ultrathin or heterojunction solar cells) and material processing to overcome these limitations in PIMs.

Concluding remarks

While tremendous progress has been made over the past 5 years with regard to the development of lead-free perovskites and perovskite-inspired materials, significant work remains to be done to unlock their potential as solar absorbers. Initial investigations in this area have shed some light on intrinsic limitations (e.g. strong phonon coupling, high exciton binding energies) to PIM performances, beyond the extrinsic factors such as microstructure and defect-related bottlenecks. However, much work is still needed to understand the origin and relative extent of these limitations. Questions regarding the nature of phonon coupling and the role of short-range interaction in inducing localized states remain open. Furthermore, assessing the presence and effectiveness of defect tolerance in these materials will undoubtedly benefit this field. Crucially, given the large compositional space available for PIMs, in answering these questions, the field should aim at developing composition-property relations for these materials. Therefore, identifying fingerprints for the most promising PIM structures and chemistries, capable of overcoming localization and deep-trap recombination issues, is a high-priority goal in the short term. To achieve this, a combination of advanced characterization techniques will no doubt prove beneficial. Photoconductivity probes, in particular, have the potential to give photophysical insights directly correlated with the operation of PIMs in solar cell devices. In order to achieve high efficiency device performances, however, significant advances in mastering extrinsic aspects, such as microstructure, lattice ordering, and electronic energy landscape, are required in the longer term. We envision that advanced structural characterization (e.g. STEM, nBED) and photocurrent-based characterization (e.g. PCS, TPV, TPC) will be crucial in enabling this, thereby spurring the development of PIMs as highly efficient lead-free solar absorbers.

Acknowledgments

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8. Operando characterization techniques for lead-free perovskite and derivatives-based photoelectrocatalysts

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Status

Operando techniques are powerful tools in PEC research for studying the structural, morphological, and compositional variations of materials in real-time, under the same conditions they experience during operation. Compared to conventional ex-situ characterization, which occurs before and after the PEC process, *operando* methods enable the tracking of transformations under applied voltage and illumination. This provides deeper insights into the fundamental mechanisms that govern the device's performance and stability.

While operando methods are well established in electrocatalysis, their application in PEC remains limited, primarily due to challenges of incorporating illumination into the experimental setup. These techniques have gained interest in PEC research, especially for transition metal oxide-based photoelectrodes, known for their high stability [182, 183]. For halide perovskites and their derivatives, which operate under light and in an electrolyte environment, *operando* studies are especially important [184, 185]. These materials, being ionic and structurally soft, are prone to dynamic structural transformations and chemical reactivity under operating conditions, which can significantly impact the optoelectronic properties and long-term stability. A more detailed understanding of the driving processes in PEC systems, the formation of hydrated intermediates and the degradation mechanisms (e.g. photocorrosion and loss of perovskite structure) is critical for developing stable and efficient PEC materials [114, 186, 187].

A key feature of *operando* techniques is the use of non-destructive probes, which allow for monitoring modifications induced by operating conditions rather than any probe-material interactions. In a PEC three-electrode set-up, *operando* techniques can be used to (i) characterize material properties and (ii) study charge carrier dynamics (see schematic in figure 10).

To analyse surface morphology changes and the electrode/electrolyte interface, tip-based techniques such as SECM are typically employed [188]. Raman spectroscopy, when used in-*operando*, can offer valuable insights into the structural changes of the material and generated products, though its effectiveness depends on whether the products reach detectable concentration levels and exhibit Raman-active modes [189]. X-ray based techniques such as XAS, XPS and XRD are particularly valuable for obtaining information regarding the local order around selected atomic species, valence states, crystalline phases, particle size, phase transitions, and crystallite dimensions [182, 190]. Beyond material characterization, understanding charge dynamics is crucial for optimizing photoelectrode design. Techniques that introduce small perturbations to the *operando* steady state of light illumination and applied voltage have garnered significant interest, as they linearize the mathematical description of non-linear processes. This ultimately simplifies the analysis, particularly in the frequency domain, where resolving information over a range of timescales is generally easier compared to time-domain measurements.

Current and future challenges

By investigating PEC systems under *operando* conditions, three key challenges need to be addressed: (i) technical limitations, (ii) material stability and probe tolerance, and (iii) difficulties in the analysis and interpretation of the obtained data.

The primary technical challenge is the integration of the PEC set-up with the sample chamber of the selected technique, with minimal interference in the measurements. This often requires custom-designed PEC cells, where achieving optimal illumination conditions can be particularly challenging. Additionally, other challenges such as bubble formation, electrolyte refreshment, or gas accumulation at the electrode/electrolyte interface must be considered during the design of the *operando* experiments.

For tip-based techniques, the effects of light reflectance and scattering from the tip need to be accounted for. Furthermore, the tip size is a crucial factor that determines the spatial resolution at the nanoscale level [191]. In x-ray-based techniques, it is essential to consider the energy of the x-ray probe and experimental mode, accounting for the total x-ray absorption of the whole system, including the

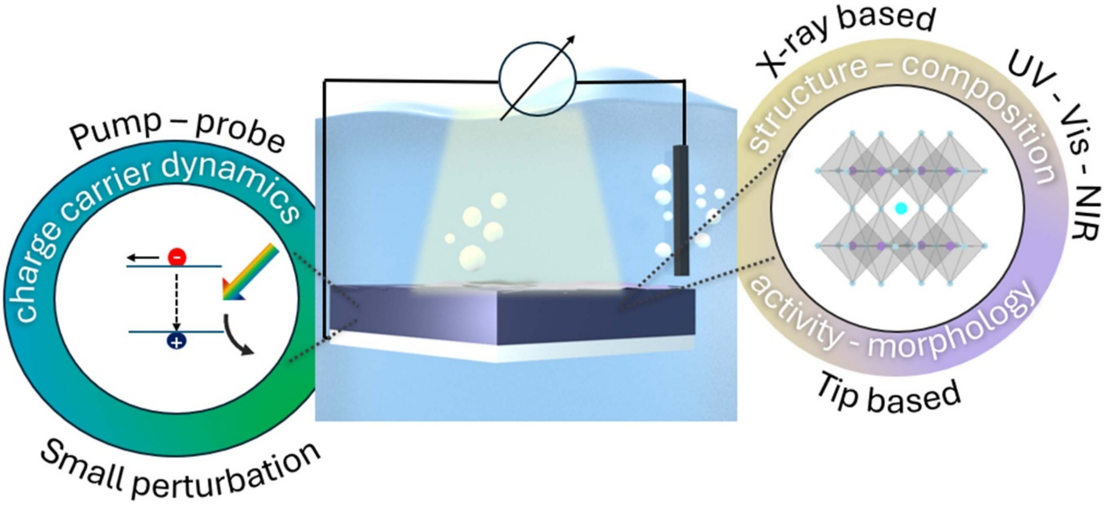

Figure 10. Schematic representation of PEC operando techniques, based on the nature of the probes. These techniques can be used to study either the charge carrier dynamics (pump-probe and small-perturbation techniques) or the material properties of the photoelectrode (x-ray, UV–Vis-NIR, and tip-based methods).

electrolyte. This is crucial when dealing with devices that feature complex architectures, where the perovskite absorber is sandwiched between electron and HTLs [192]. In this framework, the use of hard x-rays is generally favoured, despite the associated partial reduction in surface selectivity [190]. In general, *operando* XPS for PEC systems is more complex than hard XAS, primarily due to the difficulties associated with the operating conditions, such as the incompatibility of vacuum with the liquid environment required for PEC measurements [182].

Ensuring the non-destructive nature of the probe is especially critical for materials with low thermal stability such as perovskites. This is a concern when using high-flux radiation, e.g. x-rays generated by a synchrotron, where long exposure times (often necessary for obtaining a high signal-to-noise ratio) may lead to degradation [193].

The strong photoluminescence of perovskite materials can complicate *operando* Raman measurements, as the fluorescence signal can overlap with the Raman signal. Addressing this issue requires improving the signal-to-noise ratio, preventing material degradation due to the high laser energy and maintaining optimal illumination conditions without saturating the detector [194].

Finally, advanced models are required that are sufficiently complex to capture the device physics of these systems (e.g. accounting for electron extraction, interface recombination, etc), but also allow relative simplicity in the data analysis to allow the separation of different processes and determine related parameters [195, 196]. These models should ideally be compared against full drift-diffusion simulations to confirm their validity in specific conditions or under the chosen assumptions, while also ensuring they maintain consistency across different steady-state and transient measurements [196].

Advances in science and technology to meet challenges

To extend the *operando* approach to PEC systems, there is a need for advanced spectroscopic instruments, possibly capable of supporting multiple approaches, alongside the development of fundamental models to establish a holistic understanding of the device operation.

In SECM, probe engineering will be crucial for enhancing resolution at the nanoscale. Additionally, controlling the experimental environment (e.g. humidity and temperature) is essential to ensure reproducibility in long-term measurements [197]. To improve the stability of Raman spectroscopy for *operando* studies, careful selection of laser intensity, wavelength and measurement duration is crucial [189].

The inclusion of detailed descriptions of experimental set-ups in publications will help to accelerate the use of *operando* XAS for photoelectrodes. To address the technical challenges outlined in the previous section, research efforts are focused on developing adaptable PEC cells that ensure a leak-free environment [198]. Key considerations include sample composition, thickness, matrix and the energy range needed for XAS at specific edges. To minimize sample damage, especially with high-flux undulator radiation, beam rastering using a translational stage is recommended. The experimental design must also account for light intensity and sample stability under the beam, particularly for processes with low cross-sections [190]. The development of NAP-XPS has also made significant progress, enabling *operando* XPS through methods like 'dip and pull', 'tilted sample' and 'capillary' [194, 199, 200]. Although this technique is less widely used in *operando* mode than XAS, its surface sensitivity (due to the short mean free path of electrons) provides valuable insights into the electrode/electrolyte interface, which is critical in photoelectrocatalysis.

Due to the slow kinetics associated with many of the most challenging reactions driven by PEC systems, a wide timescale (from picoseconds to seconds) must be explored using pump-probe techniques e.g. TAS, or small perturbation techniques, i.e. IMPS and IMVS or TPC and TPV [201].

These operando studies in the time and frequency domain are particularly useful for investigating perovskite materials integrated into complete devices with selective transport layers, revealing ion migration, electron injection and recombination processes [184, 185]. To this respect, a unified and consistent model for interpreting small-perturbation measurements is essential. Such a model should account for the dynamics of charge carrier recombination, transport and extraction of both electrons and holes, in the bulk material and at the interfaces [196]. While this approach is adopted in the solar cell community, it is less common in photoelectrocatalysis, leading to misinterpretations of device physics. Accurate modelling of the device physics is key to identifying the factors that limit the device performance and designing effective mitigation strategies.

Concluding remarks

Environmentally-friendly, lead-free perovskite materials and their derivatives have emerged as promising candidates for solar-to-energy conversion systems, particularly as photocatalysts in combination with other semiconductors [79, 202, 203]. *Operando* characterization methods provide a deeper understanding of the complex interplay between material properties, reaction mechanisms and device performance when these materials are used as photoelectrodes. The real-time nature of these measurements provides unique insights into operational degradation mechanisms that ultimately lead to device failure. A key challenge is correlating microscopic degradation mechanisms occurring at the material level, with macroscopic device performance metrics, such as photocurrent density, onset potential and long-term stability. Additionally, investigating the fundamental processes involving photogenerated charge carriers is crucial for better understanding the transport and recombination mechanisms involved in photoelectrocatalysis, both within the bulk material and at the interfaces. This is especially important for the popular heterojunction systems, where the interaction between the materials and their respective band alignment significantly influences the performance. Elucidating the dynamics of charge carriers and the fundamental characteristics of these materials will help identify the performance-limiting factors and accelerate the development of next-generation photoelectrocatalytic systems for sustainable energy applications.

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9. Green wet-processing of lead-free perovskites and derivatives

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Status

This chapter specifically focuses on the chemical engineering aspects of lead-free perovskite processing, providing a roadmap for sustainable solvent design, precursor–solvent interaction optimization, and defect passivation strategies. The focus is on the molecular-level design of solvent systems and deposition processes tailored to lead-free materials. The aim is to establish a foundation for scalable and environmentally friendly fabrication by bridging fundamental materials chemistry with application-driven requirements. Solvent selection plays a pivotal role in perovskite processing, influencing material stability, film morphology, and overall device efficiency. Conventional solvents, such as DMF, pose toxicity risks, prompting the search for greener alternatives. A recent study, although related to conventional lead perovskites, emphasizes the effectiveness of bio-derived and water-based solvents, such as ethyl acetate and isopropanol, in improving film formation while reducing environmental impact [204].

A key factor influencing the fabrication and performance of lead-free perovskites is solvent engineering. In response of conventional solvents, bio-derived solvents, water-based systems, and ionic liquids have gained traction, offering new pathways to improve film formation, defect passivation, and material sustainability [205]. Recent breakthroughs in aqueous hybrid salt/polymer solutions and alcohol-based deposition techniques have demonstrated improved film morphology and stability, yet further advances are needed to achieve industrial viability [206]. Beyond environmental benefits, the adoption of green solvents is also crucial for scaling up lead-free perovskite technology. Techniques such as slot-die coating and blade coating have shown promise for large-area processing, but their effectiveness depends on solvent properties, drying kinetics, and precursor solubility [207]. Moreover, the recovery and recycling of green solvents remain underexplored, despite being essential for sustainable large-scale production. Computational modelling has recently emerged as a powerful tool for rational solvent design, allowing researchers to predict solvent-perovskite interactions and optimize processing conditions without relying solely on trial-and-error experimentation. Advances in DFT calculations and molecular dynamics simulations now enable data-driven selection of solvent systems, accelerating the discovery of high-performance, environmentally friendly formulations [208].

As regulatory restrictions on toxic solvents tighten, the push for scalable, sustainable, and high-efficiency lead-free perovskites will continue to grow. Future research will need to integrate computational screening, solvent engineering, and scalable deposition techniques to fully harness the potential of lead-free perovskites. The ultimate goal is to develop high-efficiency, stable, and commercially viable perovskite materials, unlocking new possibilities for renewable energy conversion, PCs, and optoelectronic devices. The selection of green solvents significantly affects perovskite crystallization, film uniformity, charge transport, and stability. Alternative solvent systems must exhibit low toxicity, high solubility for perovskite precursors, and compatibility with scalable deposition techniques. The application of these solvents varies across different processing methods and materials, requiring tailored strategies for optimal performance, as reviewed for tin-based perovskites [104].

Water-based and alcohol-based processing. Water-based processing offers an environmentally friendly approach by minimizing organic solvents. However, metal halide solubility and precursor hydrolysis present challenges. Xi *et al* addressed these issues using aqueous hybrid salt/polymer solutions, improving $FASnI_3$ film morphology and crystallization kinetics [206]. Water-based perovskite processing has gained significant interest due to its potential to replace highly toxic solvent systems, yet its widespread adoption is hindered by unpredictable solubility dynamics, hydrolysis rates, and unwanted side reactions that can deteriorate film quality. Advanced methodologies are required to further stabilize perovskite precursors in aqueous media, incorporating chelating agents or polymer-assisted stabilization techniques. Alcohol-based solvents like ethanol and isopropanol enable rapid, low-toxicity film formation. Alcohol-based

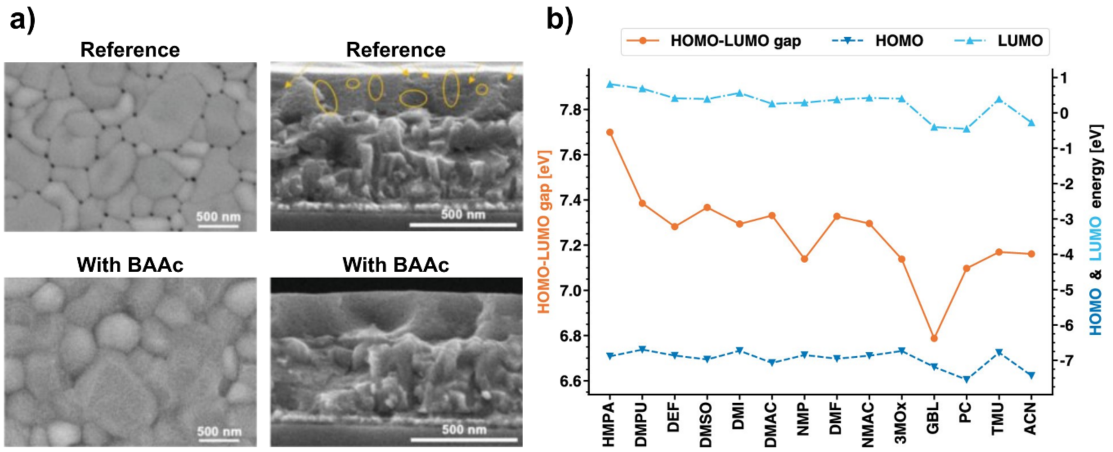

Figure 11. (a) ionic liquid (n-butylammonium acetate, BAAc) thin-film stabilization vs $FASnI_3$ reference perovskite. Reprinted (adapted) from [213]. CC BY 4.0; (b) Calculated highest-occupied molecular orbital (HOMO) and lowest-occupied molecular orbital (LUMO) energies of the 14 considered tin complexes plotted in dark and light blue, respectively, against the right y-axis and the resulting HOMO–LUMO gap plotted in orange against the left y-axis. Reproduced from [214]. CC BY 4.0.

processing methods, particularly for large-area deposition, have demonstrated enhanced solvent drying kinetics, facilitating fast film formation with minimal defects [41]. Additives incorporated into alcohol-based systems help refine grain size and improve structural integrity, leading to enhanced optoelectronic properties [209, 210]. Future work should focus on optimizing alcohol-based processing techniques to improve reproducibility and enhance compatibility with industrial-scale fabrication methods.

Bio-derived and ionic liquid solvent strategies. Bio-derived solvents such as GVL and DMI show promise for improving solubility and film morphology [211]. Their ability to coordinate with perovskite precursors facilitates homogeneous crystallization, enhancing PV efficiency, however to date to the best of our knowledge there are not directly reports on lead-free solar cell fabrication [212]. These solvents also align with sustainability goals, reducing the reliance on petroleum-based solvents and offering improved chemical compatibility with perovskite precursors. However, the structural diversity of bio-derived solvents poses challenges in optimizing their interactions with perovskite precursors, requiring systematic screening and modification of solvent properties to maximize performance. Ionic liquids also play a crucial role in regulating crystallization and minimizing defects. Li *et al* demonstrated that ionic liquid stabilization improves THP efficiency and stability, addressing common issues of degradation, where room-temperature ionic liquid capping techniques enhance perovskite thin-film stability, further extending operational lifespan [213] (figure 11(A)). Future efforts should explore hybrid solvent systems that integrate ionic liquids with alcohol-based or bio-derived solvents to achieve a balance between stability, processability, and efficiency.

Current and future challenges

Scaling lead-free perovskites from laboratory research to industrial production necessitates optimizing fabrication methods. Large-area deposition techniques such as blade-coating and slot-die coating enable uniform film formation over extensive substrates, particularly when paired with green solvents [215, 216]. However, precise control over solvent evaporation rates, precursor concentration, and substrate interactions remains a challenge, impacting film morphology and overall device performance.

Controlling evaporation rates and precursor-solvent interactions is critical to achieving reproducibility and minimizing batch-to-batch variation [217]. Further research is needed to develop adaptive processing strategies that accommodate variations in humidity, temperature, and drying kinetics to ensure consistency in film formation. In addition, innovative in-line monitoring techniques—already successfully applied to lead-based perovskites, such as optical coherence tomography and *in-situ* spectroscopy [218], can be implemented to track crystallization dynamics in real-time, facilitating process optimization in lead-free solutions.

Another key consideration for industrial scalability is solvent recovery and recycling. For lead-free perovskites, there are currently no published studies that specifically address solvent recycling strategies. However, research on general perovskite systems provides a valuable framework that can be extended to lead-free materials. Green solvent adoption must go beyond simply replacing toxic chemicals; it should also focus on minimizing solvent waste through efficient recovery systems. Recent works have demonstrated closed-loop solvent recycling and purification techniques, such as vacuum distillation, membrane separation, and adsorption filtration, which significantly reduce material costs and environmental impact while maintaining device performance. For instance, Larini *et al* [219] implemented a circular management approach using green solvents to recover and reuse materials and solvents with over 98% efficiency retention in PSCs. Similarly, Xiao *et al* [220] proposed a holistic solvent recycling strategy that enables multiple reuse cycles without compromising material quality, achieving substantial reductions in environmental footprint. Although these studies focus primarily on lead-based perovskites, the methodologies they establish are equally applicable to lead-free systems. Future research should investigate the compatibility of solvent recovery techniques with large-scale processing of lead-free perovskites, ensuring that solvent reuse does not compromise film quality or device performance while aligning with industrial sustainability standards.

Stability remains a key challenge, especially for tin- and germanium-based perovskites, which are prone to oxidation and rapid degradation [221–223]. Protective encapsulation strategies and double perovskite structures [224] have been proposed to mitigate these issues, although in the case of $Cs_2AgBiBr_6$ some source of degradation have been found in ionic diffusion [126]. The long-term stability of lead-free perovskites is also highly dependent on the interactions between the solvent system and precursor composition. Solvent-mediated degradation mechanisms, including residual solvent effects and hygroscopic instability, must be thoroughly investigated to develop effective stabilization techniques.

Advances in science and technology to meet challenges

Despite advancements, several research gaps must be addressed to fully integrate green solvents into large-scale perovskite fabrication. A comprehensive approach involving novel solvent systems, advanced deposition techniques, and improved stability strategies is essential for advancing lead-free perovskite technology.

Computational modeling for solvent optimization. The design of green solvents for perovskite processing can be significantly accelerated using computational modelling techniques [225]. Approaches such as DFT calculations, molecular dynamics simulations, and ML algorithms allow researchers to predict precursor solubility, solvent-perovskite interactions and energetics [214] (figure 11(B)). By leveraging computational chemistry, solvent systems can be rationally designed rather than relying on costly and time-consuming experimental screening. These tools can help identify the most promising solvent candidates, optimize solvent-additive interactions, and predict long-term stability outcomes. Future work should focus on integrating HT computational screening with experimental validation to establish a database of efficient, environmentally friendly solvents for perovskite processing.

Enhancing solubility and film uniformity. Solubility limitations for alternative halides like tin, bismuth, and antimony affect film quality. Advanced solvent engineering strategies, such as ligand-assisted dissolution [226] and precursor modification, should be explored to improve dissolution kinetics and prevent inhomogeneities. Additionally, computational modelling and molecular simulations can aid in predicting solvent-solute interactions, enabling rational design of solvent systems with enhanced solubility and crystallization behaviour.

Tailoring processing conditions for scalability. Deposition methods must be further refined to balance speed and film homogeneity. Hybrid techniques integrating spray [227] and blade coating may offer improved control over film thickness and crystallization rates, enabling more consistent device performance. Additionally, R2R processing techniques must be explored for continuous, scalable production of perovskite films [228]. Research should also focus on developing automated process control systems to ensure consistency and reproducibility in industrial-scale manufacturing. The first fully R2R lead-based perovskite module has been recently demonstrated by Weerasinghe *et al*, using a combination of R2R techniques: gravure for the ETL and carbon top electrode, slot-die for the perovskite and HTL and screen printing for silver charge collection grids [229]. They implemented a programmable R2R slot-die coater for automated operation, enabling the daily fabrication of thousands of unique perovskite cells, and introduced an automated R2R tester capable of assessing over ten thousand cells daily for swift analysis. Despite the groundbreaking work in the upscaling area, the process still relies on the use of DMF and chlorobenzene.

Long-term stability and environmental adaptability. Addressing perovskite degradation requires deeper investigation into solvent-induced stability enhancements. Novel solvent-polymer interactions [230], capable of passivating defects [231] and protecting against moisture infiltration, should be a focus of future research. Advanced encapsulation materials and multi-layered barrier coatings should be integrated into the fabrication process to extend device lifetimes under real-world conditions.

Expanding applications beyond PVs. Lead-free perovskites show promise beyond solar cells, particularly in PCs and PEC reactions. Their tunable band gaps and long charge carrier lifetimes make them ideal for HER and CO_2 reduction reaction [79]. Hybrid perovskite-carbon composites further enhance charge separation and photocatalytic performance [232]. Future work should investigate solvent strategies that optimize these materials for broader renewable energy applications, including artificial photosynthesis and sustainable fuel production.

Concluding remarks

Green solvent strategies play a pivotal role in advancing lead-free perovskite technologies for scalable, sustainable solar energy applications. Bio-derived, water-based, and ionic liquid solvent approaches offer promising alternatives to toxic conventional solvents. However, addressing solubility constraints, optimizing deposition techniques, and improving long-term stability are essential for commercial viability. Future advancements in computational solvent design, in-line process monitoring, and hybrid solvent engineering will further accelerate the development of lead-free perovskites as high-performance, sustainable materials for renewable energy applications.

Acknowledgments

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10. Vapour deposition of lead-free perovskites and related semiconductors

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Status

MHPs, and other semiconductors chemically related to them, can be cast into thin films using either solution-based methods, discussed in the previous chapter, or PVD techniques [233, 234]. Most of the existing research focuses on solution-processed materials, whereas vapour-deposited perovskite films and devices, the focus of this chapter, have been explored by only a limited number of research groups. This gap originates from the fact that solution-processing methods can be easily adopted in a research laboratory, but also from the commonly held perspective that these techniques could be translated to inexpensive, HT, R2R industrial coating. However, scaling solution-processing methods to industrial production remains a challenge. Also, it is important to note that the final cost of a device is typically driven by material and process efficiency, with capital equipment costs depreciated over time in industrial settings. An analogy can be found in the development of organic electronics: the only optoelectronic devices that have reached mass production are organic light-emitting diodes, fabricated exclusively by PVD methods [235]. More broadly, most semiconductors used in industrial applications are processed by PVD. For instance, CdTe thin-film solar cells, which account for approximately 5% of the global PV market, are manufactured by vapour transport deposition [236]. Therefore, advancing solvent-free PVD techniques for perovskite film and device fabrication may facilitate a more direct transition from laboratory research to industrial-scale production.

One of the key advantages of PVD methods is their ability to produce uniform layers, which is crucial for device performance and stability. Moreover, these techniques do not suffer from solvent residuals, allowing for better control over film composition, density, crystallization, and thickness. However, scaling up these methods presents certain challenges, which will be discussed in later sections.

Figure 12 provides an overview of PVD techniques reported for the preparation of perovskites and related materials. They include variants of thermal sublimation—such as co-evaporation, sequential evaporation, CSS, and flash evaporation—as well as plasma-based methods like sputtering and PLD. Although ALD is a CVD technique, it is included here due to its vapour-phase nature and its growing industrial relevance, particularly in its HT form, spatial ALD. Among these methods, evaporation and sputtering are the most widely adopted in industrial optoelectronic device fabrications, though not yet extensively for halide perovskites. Figure 12 also summarizes typical deposition rates and average substrate temperature for each technique, and it highlights those that require pre-synthesized perovskite targets—namely flash evaporation, sputtering, and PLD. Notably, most of these techniques have been used to process perovskite films and integrate them into functional devices, with the exception of ALD.

Despite their industrial viability, vacuum-based techniques still face challenges such as deposition rate limitations, high equipment costs, and process optimization. The following sections will explore these challenges and potential solutions.

Current and future challenges

Co-evaporation is a high-vacuum deposition technique in which multiple chemical precursors are simultaneously evaporated and condensed onto a substrate to form a uniform thin film. It allows for complex compositions by using multiple sources; however, maintaining precise control over each source, especially for volatile organic salts, can be challenging [237, 238]. Sequential evaporation, in contrast, deposits each component one after another, simplifying the compositional control [239, 240]. This method is compatible with inline processing, making it suitable for large-scale manufacturing. One challenge, however, is the limited chemical interdiffusion between layers, which might limit homogeneity especially in thicker films. Both co-evaporation and sequential evaporation operate at low-to-moderate deposition rates (typically 1–10 nm min^{-1}) [241].

CSS and flash evaporation offer significantly higher deposition rates (>1 μm min^{-1}) [242]. In CSS, materials are sublimed within a narrow gap between a heated source and the substrate, allowing for low vacuum [243, 244]. While low vacuum is advantageous, it also hampers the sublimation of inorganics

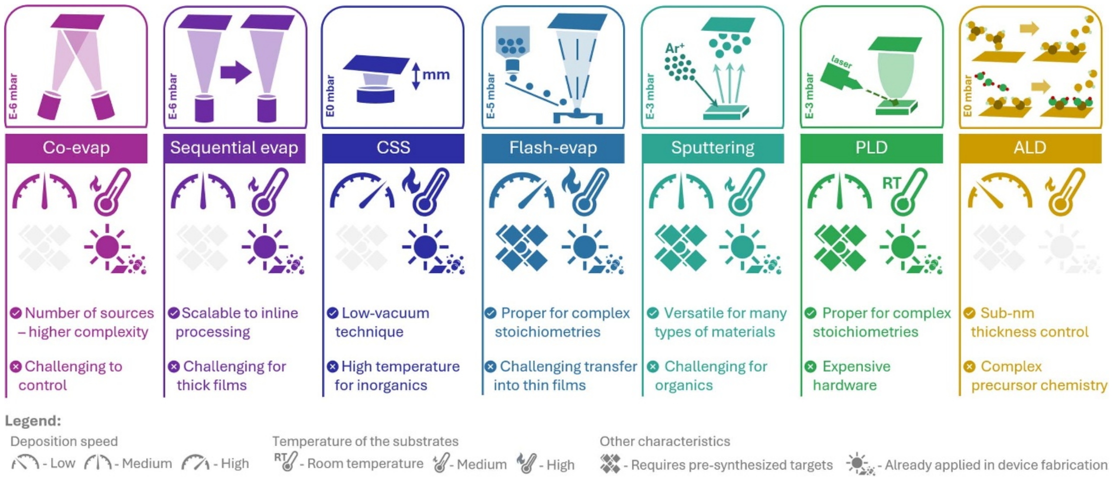

Figure 12. Overview of PVD techniques used for the fabrication of metal halide perovskite films, all using precursors in the form of powders or solid targets, except ALD that uses metalorganic precursors. The advantages (ν) and disadvantages (X) of the methods are highlighted, as well as the deposition rates, process temperature and demonstrated application in PV and/or PEC.

due to high sublimation temperatures at these pressures. Flash evaporation, on the other hand, involves rapid heating of pre-synthesized perovskite powders under vacuum to induce evaporation and condensation onto a substrate [245, 246]. This technique requires previous preparation of the materials, and the sublimation of complex stoichiometries is non-trivial due to the risk of decomposition.

Sputtering, a widely adopted industrial thin-film deposition technique, uses an energetic argon plasma to bombard a solid target, ejecting atoms or clusters that deposit onto a substrate. It is a versatile method applicable to a broad range of materials, including halide perovskites [247, 248]. Most studies on sputter deposition of perovskites employ sequential methods [249, 250], yet examples of single-source deposition, in particular for Sn-based perovskites [251], have also been demonstrated. However, it poses significant challenges when applied to organic salts and complex compositions. In contrast, PLD employs focused high-energy laser pulses to locally ablate a target, generating a plume of energetic species directed towards the substrate [252, 253]. PLD is relatively insensitive to the volatility of the target precursors, allowing for the deposition of complex material compositions, due to the non-equilibrium nature of the ablation process [254]. Both, sputtering and PLD use a solid pre-synthesized perovskite target material. Yet, while PLD ensures the integrity of the target after several depositions, sputtering can easily damage it. In both techniques, the ability to introduce background gases allows for thermalization of ejected species, minimizing damage to underlying substrate layers. Although PLD has proven effective for stoichiometric transfer of complex materials, the excimer laser cost and the deposition throughput (demonstrated deposition rates up to 80 nm min^{-1}) [255] remain significant barriers for large scale manufacturing.

ALD offers exceptional conformality and precise thickness control by sequentially introducing gaseous precursors in the chamber in self-limiting reactions. While ALD is well-suited for microelectronics applications that require ultrathin conformal layers, its low deposition rates, and the highly reactive precursors, make it not yet compatible with perovskite optoelectronics. Although perovskite films processed via ALD have been explored, they have yet to be successfully implemented in optoelectronic devices [256].

Advances in science and technology to meet challenges

To fully unlock the potential of PVD techniques for halide perovskite fabrication and scale them for industrial applications, significant advances in both scientific understanding and technological development are required. Greater community-wide efforts toward vacuum and vapour-based growth are essential to achieve the level of maturity seen in solution-processed approaches, particularly in areas such as growth mechanisms, additive engineering, and methodological diversity. Potential scientific and technological advances to address these challenges are discussed below.

Scalability and deposition rates: increasing deposition rates to the micrometre-per-second range is crucial to enhance throughput and make vacuum deposition competitive with solution-based R2R techniques.

Linear vapour-deposition sources: developing linear evaporation/sputtering/ablation sources for halide materials is essential for achieving uniform precursor deposition across large substrates and move to in-line production. This, together with uniform substrate heating (when needed), should ensure homogeneity over meter-scale areas, resulting in improved material quality and facilitate large-scale production.

Cost-effective deposition equipment: various PVD techniques, such as PLD, remains cost-prohibitive for large-scale manufacturing. Reducing the cost of specialized equipment without compromising film quality is critical for widespread academic and industrial adoption of vapour-phase growth of halide perovskites.

Nucleation and growth mechanisms, particularly the influence of substrate chemistry, growth kinetics, and their correlation with film stoichiometry and microstructure development, remain largely underexplored in the literature. The implementation of *in-situ* monitoring tools for chemical, physical, and optoelectronic characterization during film formation will be critical for advancing controlled growth and deepening our understanding of vapour-deposited perovskites.

Specific to lead-free perovskites: the search for lead-free alternative semiconductors led us to new materials with complex compositions, including double perovskites (e.g. $Cs_2AgBiBr_6$) [86], vacancy ordered perovskites (Cs_2SnI_6) [257] and chalco-halide compounds (Ag_2SI, AgBiI, AgIS) [258, 259]. Mainly the dissimilar volatilities of the chemical precursors (e.g. iodides vs sulphides, Ag vs Bi) make the process challenging for vapour deposition. The development of more volatility-insensitive methods, or sequential approaches, is just some of the possible pathways to enable thin-film formation of new complex materials with limited toxicity.

Concluding remarks

PVD techniques offer great opportunities for the development of novel semiconductors, such as perovskites, by eliminating the use of toxic solvents and enabling a more efficient use of materials and precursors. Yet, growth of novel semiconductors using solvent-free approaches remains scarce in literature. Innovations in PVD methods, along with increased focus on growth studies will be key to enable the sustainable, reproducible and controlled deposition of perovskite and related materials for next generation solar cells.

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11. Theoretical modelling and AI for perovskite-inspired materials

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Status

Theoretical modelling has been indispensable for advancing perovskite and perovskite-inspired materials in both PVs and photo(electro)catalysis. Techniques such as DFT [260], post-DFT methods [261], and AIMD simulations [262], ClML simulations [263], or MLMD [264, 265] simulations have shed light on key properties, including electronic structures, charge transport, phase stability, molecular disorder, and degradation pathways. A central finding from DFT is the concept of defect tolerance, arising from the unique frontier orbitals in perovskites [260] These shallow defect states enable high performance, even when the materials are fabricated through relatively simple, solution-based methods. Many-body perturbation theories, like GW, have elucidated relativistic effects on band structures and light absorption [261, 265].

DFT revealed band engineering principles, showing how halide p/metal s orbital overlap determines valence band positions [266]. A careful analysis based on the projection of bands on atomic orbitals reveals also that the bottom of conduction band is made of the complementary population, halide s/metal p antibonding overlap determines conduction band position [266]. Incorporation of different monovalent cations modifies the tilting angle of halide-metal bonds, fine-tuning the band gap [267]. Modelling has also shed light on charge carrier dynamics, including electron-phonon coupling [268] defect formation energies [269], and ion migration pathways [270], helping to explain hysteresis and degradation. Theoretical insights into grain boundary effects [271] and entropic stabilization [272] have contributed to the development of passivation strategies [273] and multifunctional charge transport materials [274] for improved stability.

Theoretical work in PEC and PC systems has progressed more slowly. Nonetheless, computational studies have enhanced our understanding of reaction pathways and charge transfer dynamics at perovskite interfaces, essential for applications like water splitting and CO_2 reduction [275]. For instance, research has investigated the HER catalysed by $CH_3NH_3PbI_3$ and related halide perovskites [276]. By modelling band edge positions and adsorption energies of intermediates, these studies identify optimal strategies for improving PEC performance. Meanwhile, AIMD simulations have probed degradation mechanisms under aqueous conditions, revealing, for example, the surprising stability of DMA tin bromide [277], making it a candidate for PEC.

Despite these achievements, challenges remain. Defect tolerance in halide perovskites has not yet translated to new wide band-gap semiconductors for IPVs or PEC [278]. Universal design principles for stable, efficient, and easily processable light-harvesting materials free of hazardous or scarce elements are still lacking. The microscopic mechanisms governing charge transport across interfaces remain poorly understood. Understanding atomic-scale materials growth in solution (e.g. spin coating) or vacuum (e.g. thermal evaporation) is key. Harnessing AI-driven theoretical methods to address these gaps is essential for enabling the next generation of pervasive PV and PEC technologies.

Current and future challenges

Figure 13 highlights the major challenges for next generation lead-free perovskites and PIMs, which are discussed more in details below.

Defect tolerance for high-performance materials. A major challenge is extending the defect tolerance of halide perovskites to a broader range of materials with diverse band gaps for applications in PV and P(E)C avoiding toxic elements, like lead. The shallow defect states observed in MHPs arise from unique frontier orbital interactions, yet these properties have not been replicated in many new materials. Understanding whether defect tolerance in IV–VII semiconductors is a unique phenomenon or follow

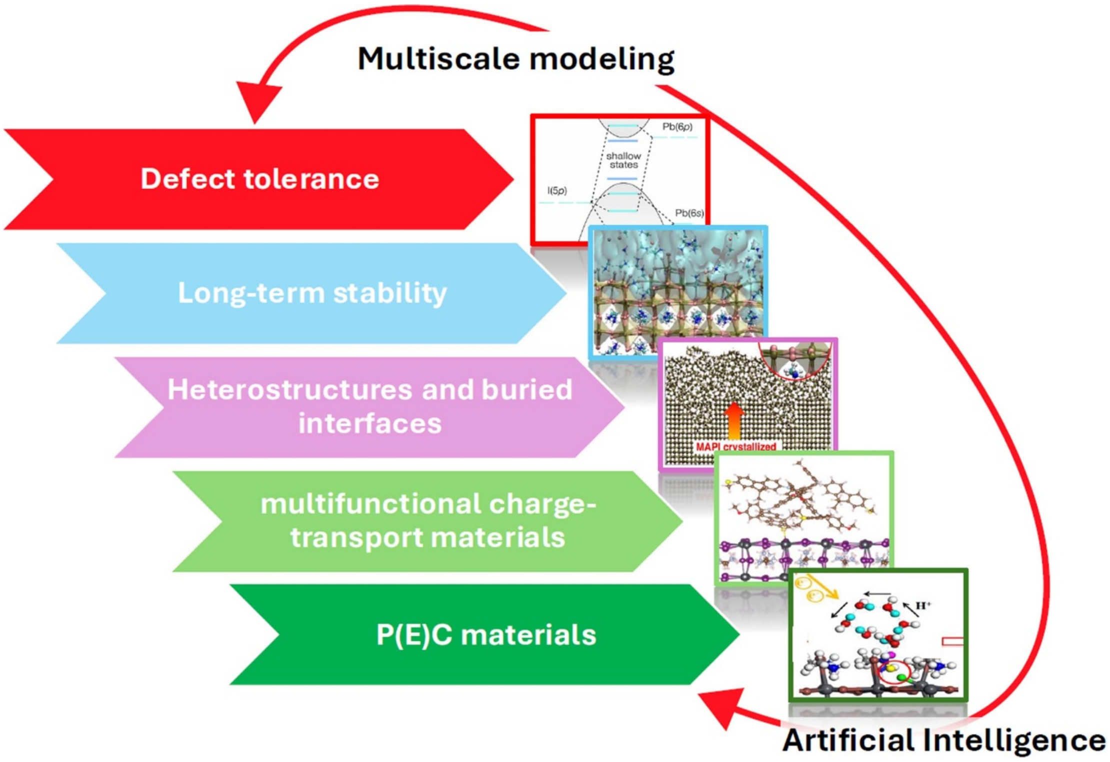

Figure 13. Visual illustration of major challenges for next-Generation lead-free perovskites and derivatives materials for photogeneration for Sustainable PV and P(E)C are divided in five categories: (i) defect tolerance, relying on the peculiar antibonding nature of the top of valence band. Reprinted (adapted) with permission from [279]. Copyright (2017) American Chemical Society; (ii) long-term stability, the ability of the material to resist to operating conditions, e.g. humidity. Reprinted (adapted) with permission from [280]. Copyright (2017) American Chemical Society; (iii) heterostructure and interfaces, which must be solid to guarantee mechanical stability, prevent the diffusion of chemical species across them, and avoid the formation of interface states that can trap charge carriers. Reprinted (adapted) with permission from [281]. Copyright (2018) American Chemical Society; (iv) multi-functional charge-transport materials, combining efficient charge extraction, barrier against diffusion of humidity and metal atoms of the electric contacts in a single element to simplify the cell stack and reduce the cost of the device; and (v) enhance water splitting in P(E)C with the help of assistance species, e.g. amine. Reprinted (adapted) with permission from [276]. Copyright (2025) American Chemical Society.

general principles is crucial. Identifying such principles would enable rational design strategies, bridging fundamental theory to technological applications.

Long-term stability. Another critical hurdle is long-term material stability under operational conditions. Materials must withstand moisture, oxygen, heat, and bias stress. Achieving this requires realistic simulations to identify degradation pathways and develop mitigation strategies, such as incorporating additives or passivating agents to slow degradation. Testing novel materials for chemical degradation, thermodynamic stability, and defect thermodynamics *in silico* is essential.

Heterostructures and buried interfaces. Efficient and cheap charge extraction materials are as important as light-absorbing ones. Charge transport across resulting heterostructures is key. Beyond macroscopic band alignment models, an atomistic understanding of heterostructure charge dynamics is required. This includes tracking wave packet diffusion and assessing the impact of bulk/interface defects, lattice mismatch–induced strain, and interfacial polarization. Accurately modelling these processes necessitates precise characterization of light-absorbing/charge-transport interfaces. Early computational studies often focused on simplified interfaces, such as those associated with the (100) surface of cubic $CH_3NH_3PbI_3$. Yet, different facets exhibit distinct behaviours, and one must identify and investigate the most relevant heterostructures per material pair. This requires predicting thermodynamically or kinetically favoured surfaces of each material and assessing their structural and chemical compatibility.

The rise of **multifunctional charge-transport materials**—serving as carrier extraction layers and protective/passivating coatings—introduces added complexity. While simplifying fabrication, these materials must meet multiple performance criteria, making their theoretical design particularly challenging.

Specific aspects of P(E)C materials. Unlike PV, PEC systems operate in dynamic and complex electrochemical environments, where reaction intermediates interact with catalyst surfaces. Developing quantum mechanical models that account for solvent effects, ion adsorption, and proton-coupled electron transfer is critical. A fundamental requirement for PEC efficiency is aligning band edges with reactant redox potentials, such as water or CO_2. However, the band structures of soft materials are highly sensitive to composition, strain, and defects. Thus, material discovery must extend beyond vacuum-based calculations to include realistic electrochemical environments, enabling accurate predictions of band alignment under operating conditions. Stability remains an even greater challenge in PEC than in PV, and overcoming degradation issues could drive major breakthroughs.

Advances in science and technology to meet challenges

HT calculations can uncover novel materials exhibiting defect tolerance and appropriate energy levels. They have been previously applied to halide perovskites, but challenges remain: PIMs are inherently soft and disordered, meaning a single configuration is insufficient. For example, the lead-halide perovskite cubic framework is 'cubic on average'—its average properties differ from those of the 'average structure'—requiring evaluation over an ensemble of configurations.

Data produced by high throughput calculation and specialized materials databases [282, 283] can be used to train surrogate property models (e.g. Gaussian-process regression). This, in turn, can be combined with explainable AI (e.g. SHAP [284]) to find the compositional or structural characteristics driving key properties of PV (PEC) materials and, in a closed-loop workflow with generative models [285], produce new materials optimized for them.

Standard DFT struggles with shallow defect states, necessitating the use of hybrid functionals, the GW approximation, and spin–orbit coupling for reliable accuracy, while BSE is needed to capture excitonic effects. These requirements significantly increase the cost of HT screening. AI-driven predictive models offer a promising approach to narrow the search space and extrapolate GW-level accuracy from DFT data, refining only promising candidates.

Modelling heterostructures presents further challenges. These may be out-of-equilibrium systems, with atomic-scale morphology and stability depending on growth conditions. Soft materials often exhibit structural differences at operating temperatures compared to geometry-optimized predictions. Realistic models require thousands of atoms and the ability to simulate atomic-scale formation processes. AIMD could be used but is computationally expensive, while ClMD—used, for example, to simulate hybrid perovskite growth [281]—lacks generality and accuracy. Foundational ML potentials can bridge this gap, followed by *ab initio* refinement in a multiscale approach focused on selected systems. This also enables screening of defect distributions—determining whether they accumulate at interfaces or reside in the bulk—which critically impacts transport properties. Promising heterostructures, selected using heuristics such as bulk and local band alignment, can then be studied for electron transport using advanced methods, such as the Bloch-Boltzmann approach in the relaxation time approximation, time-dependent DFT, or non-equilibrium Green's function. MLMD or AIMD simulations, assisted by enhanced sampling, can determine hydrophobicity, diffusion coefficients, and healing of surface defects to assess multifunctional charge-transport materials.

Results from atomistic level calculations can be used for multiscale modelling of the entire device. Early attempts focusing on the sole absorbing layer date back to 2014 [286]. A more extensive hierarchical multiscale modelling of the entire device should consist in a workflow that from DFT calculations determining band offsets, dielectric constants and defect formation energies to be fed into kinetic Monte-Carlo and drift–diffusion solvers, reproducing hysteresis, ion migration and light-bias degradation in complete perovskite stacks. Some first demonstrations of such DFT → MLMD → mesoscale → TCAD pipelines to design high-performance PV cells recently emerged [287, 288].

In PEC systems, explicit solvation models—augmented by implicit schemes like Poisson–Boltzmann—are crucial for simulating realistic electrochemical environments. Accurate band-edge alignment with redox potentials requires high-quality electronic structure calculations including solvent interactions, ion adsorption, and proton-coupled electron transfer. Hybrid quantum-classical approaches that combine electronic structure theory with molecular dynamics, along with predictive models to refine DFT energy levels, are essential. Understanding PEC mechanisms, through enhanced sampling accelerated by multiscale and AI techniques, is critical for designing co-catalysts that improve the performance and stability of perovskite-inspired materials.

This summary shows how AI, multiscale modelling, and enhanced sampling techniques can unlock the power of computation to drive progress in the field.

Concluding remarks

In conclusion, the integration of advanced theoretical modelling and AI-driven approaches will give a significant contribution to the discovery and optimization of next-generation lead-free perovskites and derivative materials for sustainable PVs and photo(electro)catalysis. HT calculations, when combined with AI-enhanced predictive models, enable rapid screening of defect-tolerant materials and precise tuning of electronic properties. Moreover, multiscale and enhanced sampling methods will allow one to model the realistic morphology or even the synthesis of complex heterostructures based on soft or disordered systems. Inclusion of specific solvent, enabled by hybrid quantum-classical techniques, will push the understanding of PEC systems and the mechanisms of reactions they promote. These technological and methodological advances address key challenges, such as defect management, stability under operational conditions, interfacial charge dynamics, and designing of robust co-catalysts that can significantly improve PEC device performance. Together, these efforts will drive the development of efficient, environmentally friendly energy solutions, continuing the progress towards a sustainable energy future.

Acknowledgments

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12. Sustainability and life cycle assessment for lead-free perovskites

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By focussing on lead free devices this road map highlights the drive to remove toxic materials from a new generation of photo-generative devices. This particular focus on 'lead free' is due to risks to human health of lead and the use of it in a soluble form which can make it more susceptible to unplanned exposure. In the UK and Europe the use of lead is restricted by RoHS (Directive 2011/65/EU) regulations to less than 0.1% of any homogenous material within the product. PV panels, assembled and installed by professionals for permanent use, are currently exempt from the RoHS directive. However, this consideration does not extend to solar cells embedded in consumer electronics or portable systems. Where devices utilize lighter flexible substrates, such as those used in IoTs applications, lead may become too great a proportion of the mass of the device to meet regulatory requirements. Furthermore, in the recent EU framework of safe and sustainable by design (SSbD), lead is included under the H1 criterion [289], prioritising its replacement as it appears on the candidate list of SVHC for authorization and is classified as toxic for reproduction in category IA (Harmonized classification—Annex VI of Regulation (EC) No 1272/2008, CLP Regulation). Although lead toxicity issues can be mitigated through encapsulation and recycling techniques, in the case of recycling, research into low-energy and cost-effective methods for lead extraction and purification from perovskite modules will be crucial [290].

In response to these concerns, various substitutes for lead in the absorber layer of halide perovskites have been investigated, including isovalent Sn(II), Ge(II), and divalent transition metals (e.g. Cu, Fe, Zn), as well as heterovalent elements like Bi(III), Sb(III), Sn(IV), Ti(IV), and double cations of Ag(I)Bi(III) [291].

There is no doubt that lead ions can cause harmful effects in mammals with chronic exposure. However, recent research regarding acute exposures has prompted a re-evaluation of the toxicity of other precursors compared to lead iodide, such as SnI_2, FAI, and MAI [292]. So far, the acute toxicity of BiI and CsI has been shown to be lower than that of PbI_2. Other metals such as antimony and silver are currently under evaluation by the European Chemicals Agency. Therefore, simply substituting lead is insufficient to ensure that lead-free perovskites are fully environmentally friendly.

Current and future challenges

Assessment of sustainability is usually undertaken by performing a full impact LCA. LCA of lead-free perovskites are still scarce (e.g. [141, 293, 294]) compared to those examining lead-based perovskites, as highlighted by their recent reviews [295–299]. Whilst the focus for PV perovskites starts with energy payback and CO_2 emissions, focus on other impacts such as materials utilization, land use, water and toxicity are also important [294–298]. It should be noted, however, that current characterization methods like USEtox (version 2.14) lack human toxicity characterization factors for several metals that could be present in lead-free perovskites, such as tin, bismuth, germanium, and caesium. Furthermore, a thorough review of existing factors is necessary to align them with recent toxicological research. Consequently, comparing the toxicity of lead-based perovskites with that of lead-free alternatives at the LCA level is extremely risky, and the results of toxicity categories in the LCA should be interpreted with considerable caution.

Sustainability should encompass not only environmental aspects but also ethical and social implications, which are particularly pertinent during the raw material extraction phase (e.g. Bi, Sb, Cs). To achieve this, environmental assessment studies can be enhanced through consequential LCA and the examination of multiple scenarios. In addition, sustainability analysis can be complemented by other methodologies, such as criticality analysis, circularity assessments, life cycle costing, and social life cycle assessment. This approach can help identify potential trade-offs between environmental benefits and social costs, guiding decision-makers towards more responsible practices and ultimately leading to more sustainable product development.

For many years researchers have debated whether the presence of lead will be detrimental to the commercialization and how they compare with 'lead free' alternatives. Schileo and Grancini [13] presents the argument that '*the advantages of using lead in PV panels—when including proper encapsulation and*

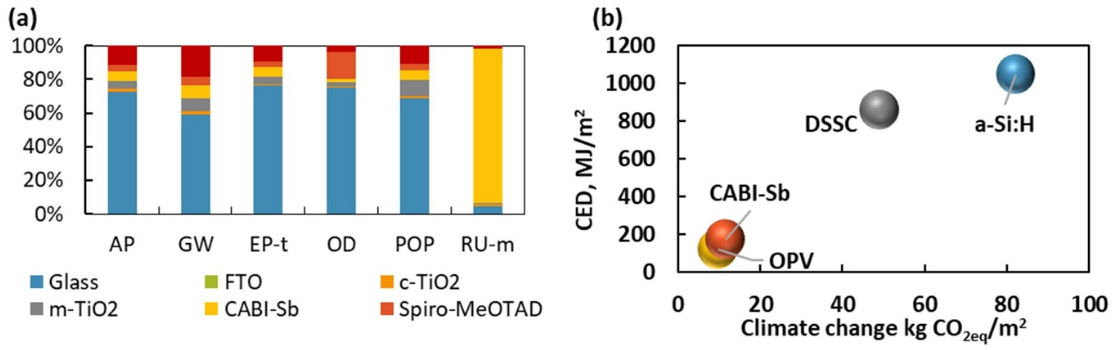

Figure 14. (a) Breakdown for CABI-Sb solar cell of the environmental impacts calculated using EF 3.1 method by layers for the impact categories of acidification (AP), global warming (GW), terrestrial eutrophication (EP-t), ozone depletion (OD), photochemical smog (POP), and mineral resource use (RU-m). (b) Comparative climate change and CED from cradle to gate for lead-free indoor photovoltaic technologies. Reproduced from [141]. CC BY 4.0.

recycling—outweigh the risks associated with its manufacturing.' Additionally, various authors have contended that the significance of the absorber layer on environmental impacts is minimal (reviewed in [299]). The most notable impacts are attributed to gold electrodes, which are commonly used in laboratory-scale research. When replaced with alternative electrodes such as aluminium or carbon, glass substrates with transparent conductive oxide become the materials with the highest environmental impacts, as illustrated in figure 14(a) for $Cu_2AgBi_{0.9}Sb_{0.1}I_6$ (CABI-Sb) perovskites [141, 300].

As discussed in chapter 9 the appropriate selection of solvents for the deposition of the perovskite layer significantly influences the efficiency of the solar cell, but it also has a considerable effect on environmental impacts. DMF, the most used solvent, is listed as SVHC and is included in criterion H1 of the SSbD. To ensure the sustainability of lead-free perovskites, it is essential to seek less harmful solvents. Similar to metals, an added challenge is the proper inclusion of their characterization factors for toxicity categories in LCAs [301].

Whilst materials selection and green solvents can reduce environmental impact, the two biggest drivers are PCE and lifetime, as outlined in chapter 2. From cradle to gate, lead-free perovskites exhibit promising results compared to other emerging PV technologies, as shown in figure 14(b). However, lead-free perovskite materials typically have lower PCE and shorter lifespans [302], and unless the application has specific lifetime constraints (e.g. single-use satellite applications [300]), this may also increase environmental impacts.

Advances in science and technology to meet challenges

The enhancement of PCE and the improvement of stability to extend the lifespan of lead-free perovskites are covered within previous sections of this roadmap, and is the critical focus to enable lead free devices to compete. Lower impact TCS have been pursued for solar cells and other applications such as displays and smart phones [303].

Promoting the circularity of lead-free perovskites through recycling and remanufacturing will prevent environmental harm from the leaching of metals and other harmful substances that can occur due to poor EOL management [290, 304]. Additionally, circularity presents the opportunity to recover critical materials such as Sb, Bi, and Ge, which are included in the EU's critical materials list [305]. Cs should also be recycled, although it is not currently included on that list due to a lack of official information, despite its potential criticality [306]. Just as with the deposition of perovskite layers, the identification of truly green solvents is crucial, necessitating detailed inventory modelling and the provision of toxicity characterization factors [301].

Concluding remarks

There are competing views on whether lead-based perovskite photogeneration devices can meet the regulatory requirements. Lead free perovskite devices are promising emerging photogeneration technologies, although it is critical that the efficiency and the lifetime are increased, which will reduce costs alongside environmental impact.

For the sake of sustainability, it is essential to reduce the impacts of TCS, avoid electrodes made from high-impact materials such as gold, optimize scaling processes, promote circular alternatives at the end of life, and utilize green solvents for both layer deposition and recovery processes at EOL.

In addition to the scientific challenges associated with improving the efficiency and stability of lead-free perovskites—which will enhance their sustainability—there are also methodological challenges in accurately assessing sustainability. This involves develop new toxicity characterization factors for LCA studies integrating findings from toxicological research, concerning emissions of metals, solvents, and other chemicals used to.

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Data availability statement

No new data were created or analysed in this study.

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