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Lead-free perovskite-inspired semiconductors for indoor light-harvesting – the present and the future

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Are lead-free perovskite-inspired materials (PIMs) the wise choice for efficient yet sustainable indoor light harvesting? This feature article outlines how wide-bandgap PIMs can provide a positive answer to this compelling question. The wide band gaps can hinder sunlight absorption, in turn limiting the solar cell performance. However, PIMs based on group VA of the periodic table can theoretically lead to an outstanding indoor power conversion efficiency up to 60% when their band gap is ~ 2 eV. Yet, the research on PIM-based indoor photovoltaics (IPVs) is still in an early stage with highest indoor device efficiencies up to 10%. This article reviews the recent advancements on PIMs for IPVs and identifies the main limiting factors of device performance, thus suggesting effective strategies to address them. We emphasize the poor operational stability of the IPV devices of PIMs being the key bottleneck for the vast adoption of this technology. We believe that this report can provide a solid scaffolding for further researching this fascinating class of materials, ultimately supporting our vision that, upon extensive advancement of the stability and efficiency, PIMs with wide bandgap will become a contender for the next-generation absorbers for sustainable indoor light harvesting.

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The urge to self-power the wireless Internet of Things (IoT) ecosystem in a cost-effective and sustainable way has recently led to a growing demand for indoor photovoltaics (IPVs).¹ Among the various emerging IPV technologies, e.g., hydrogenated amorphous silicon (a-Si:H), dye-sensitized solar cells (DSSCs)

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Currently, her research focus is on combining material focussed innovation with that of the emerging huge technologies such as the Internet of Things (IoT) and Wearables to positively contribute to achieving the big target of 'Energy Sustainability'.



substantial toxicity risk and causes concerns for their recycling.^{6,7} Therefore, it is important to develop IPV materials that do not pose any threat to the environment or health during and after the lifecycle of the photovoltaic cells. Low-toxicity tin (Sn)-based perovskites led to PCE(i)s approaching 15%.^{8,9} However, Sn-based perovskites possess a few drawbacks, including the air-oxidation of Sn²⁺ to Sn⁴⁺.^{10,11} Efforts are continuously made to suppress the Sn²⁺ oxidation. Yang *et al.* demonstrated a PCE(i) of 12.81% with a V_{OC} of 0.65 V by incorporating catechin with a hydroxyl functional group (as a doping agent) into Sn-based IPV devices to prevent Sn²⁺ oxidation and improve film morphology.¹² The highest performing (PCE(i) of 17.57% under 1062 lux) Sn perovskite device was achieved *via* interlayer passivation with KSCN-based materials, where K⁺ and SCN⁻ ions passivated both bulk and interface defects.¹³ The IPV device retained 80% of the original PCE(i) after 1200 h of



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Fig. 1 (a) Radiative-limit (RL) curve (taken from³) under indoor lighting conditions as a function of the band gap. The PCE(i) values of PIMs under WLED illumination at 1000 lux are also represented in the same figure. (b) Crystal structures of BiOI and $\text{Cs}_3\text{Sb}_2(\text{Cl}_x\text{I}_{9-x})$, adapted from³ and CABI (reproduced from²⁴). (c) Comparison between the EQE of BiOI and $\text{Cs}_3\text{Sb}_2\text{Cl}_x\text{I}_{9-x}$ devices with the WLED, FL, and AM 1.5G spectra (left), reproduced from³ and the normalized EQE spectrum of a CABI device along with the AM 1.5G and WLED emission (color temperature: 4000 K) spectra (right).

storage in darkness in an inert gas atmosphere. But the stability of Sn-perovskites in air is still not sufficient for any practical application.¹² Furthermore, their typical band gap values (~ 1.3 V) are much lower than those desired for IPV (~ 2 eV).¹⁴ Perovskite-inspired materials (PIMs) comprising air-stable Group VA cations, such as antimony (III) (Sb^{3+}) and bismuth (III) (Bi^{3+}), have recently emerged as promising wide band gap absorbers with low toxicity. The Bi- and Sb-halides and chalcogenides display similar electronic structures as LHPs.¹⁵ Both Sb^{3+} and Bi^{3+} possess the valence electronic configuration of $6s^2$, like Pb^{2+} . In addition to low toxicity,¹⁶ a high dielectric constant of these ions due to their highly polarizable nature may suppress the defect formation probability in the band gap regime.^{15,17}

These materials typically crystallize in two-dimensional or layered structures (see the crystal structures of BiOI , $\text{Cs}_3\text{Sb}_2\text{Cl}_x\text{I}_{9-x}$, and $\text{Cu}_2\text{AgBiI}_6$ (CABI) in Fig. 1b) and own band gaps in the 1.9–2.0 eV range.^{3,18} Their adoption as absorbers in single-junction solar cells led to modest efficiencies up to 4%¹⁹ mostly due to their wide band gaps, non-ideal for outdoor sunlight absorption. However, these large band gaps could be beneficial for applications in tandem solar cells and IPV. This research is

in its early infancy with only a handful of examples of PIM-based IPV (Table 1) and with still no PIM-based tandem cells reported.¹⁸

Current research and outlook on PIM-based IPV

As shown in Fig. 1a, the wide band gap values (~ 2 eV) of PIMs ensure an enhanced photovoltaic performance under indoor vs. outdoor lighting conditions. The suitability of the wide band gap PIMs for IPV can be corroborated by the great match between the external quantum efficiency (EQE) spectra of these materials and the WLED and fluorescence lamp (FL) spectra with respect to the AM 1.5G (1-Sun) spectrum (see Fig. 1c). The PCEs of the photovoltaic devices based on BiOI and $\text{Cs}_3\text{Sb}_2\text{Cl}_x\text{I}_{9-x}$ were enhanced from $\sim 1\%$ under 1-Sun to 4–5% under indoor light sources, as demonstrated by Peng *et al.* in their first IPV study on PIMs in 2021.³ Though both the materials have bandgap values slightly larger than 1.9 eV, the corresponding IPV devices yielded moderate V_{OC} values of



The self-trapping can be tuned by modifying the local symmetry of the polyhedra involving carrier-trapping.³³ Recently, we hypothesized the reduction of self-trapping in CABI by the partial alloying of some of the bismuth (III)-sites with antimony (III) ions, which leads to the local symmetry enhancement at the octahedral lattice sites of CABI.²⁶ However, to unequivocally prove the increase in the number of free carriers in CABI-Sb through the lowering of the number of STEs, advanced studies like optical-pump tera-hertz-probe (OPTP) spectroscopy, should be performed^{30,34} The suppressed carrier self-trapping in CABI through Sb alloying enabled a significant enhancement of the J_{SC} value of the corresponding IPV device. Similarly, mixing of the A-site of $Cs_3Sb_2I_9$ with methylammonium and formamidinium ions resulted in a nearly undetectable luminescence signal,³¹ unlike the weak self-trapped exciton emission observed for the pristine $Cs_3Sb_2I_9$.³⁵ The cation mixing remarkably contributed to increase the PCE(i) of Sb-based IPV's from 4.9% to 6.4%.^{3,31} These observations suggest that compositional engineering holds a

great promise to alter the symmetry of the lattice points involved in the self-trapped exciton (STE) process and diminish carrier trapping-related non-radiative losses in PIM-based photovoltaic cells. In addition, the compositional engineering was proposed to increase the mobility of charge carriers by reducing their effective masses in $\text{Cs}_2\text{AgBiX}_6$ ($X = \text{Br}, \text{Cl}$).³⁶

Open circuit voltage (V_{OC}) losses should be minimized

The theoretical optimum bandgap for IPVs 1.9–2.0 eV, and the highest predicted V_{OC} is 1.4–1.5 eV.^{37,38} However, there are only a few reports on halide perovskite photovoltaics with the experimentally observed V_{OC} of >1 V under indoor lighting conditions (1000 lux).^{39,40} Both reports are based on conventional LHP compositions (*i.e.*, CsPbI_2Br and $\text{CH}_3\text{NH}_3\text{PbI}_{2-x}\text{BrCl}_x$).

A systematic comparison between the optical bandgap (~ 1.8 –2.0 eV) of the PIMs and their reported V_{OC} values (0.5–0.6 V) under indoor illumination reveals that the PIM compositions suffer a high V_{OC} loss of ~ 1.3 –1.4 V (Fig. 2), which is huge compared to what has been reported for the LHP devices under 1-Sun illumination (less than 0.5 V). A voltage loss of ~ 0.2 V is expected and systematically observed while comparing the V_{OC} of LHP devices under indoor and 1-Sun illuminations due to the differences in light intensity. To maximise the IPV efficiency of these PIMs, it is essential to reduce the difference between the bandgap and the observed V_{OC} .

Recently, Bahadani⁴¹ has quantified the different energy losses in IPVs considering GaAs and GaInP as test cells and a warm WLED as the illumination source. For all the cases, the highest energy loss was due to the thermalisation losses (30–40%) and to the junction loss (20–30%). However, these cells demonstrated relatively low non-radiative recombination losses (~ 4 to 8%).

For the photovoltaic devices in general (and specifically for perovskite solar cells), three different voltage loss pathways (due to Shockley–Queisser limit, radiative losses, and Shockley–Read–Hall (SRH)-type losses) have been previously reported.^{42–46} Recently, Dong *et al.*⁴⁷ have quantified these losses for perovskite

solar cells ($\text{Cs}/\text{FA}/\text{MA}$ -LHP) as 273 mV, 3.12 mV, and 250.07 mV (for 1-Sun illumination), respectively. In the case of halide perovskites, the typical trap density of the order of $\sim 10^{15} \text{ cm}^{-3}$ is comparable to or slightly lower than the typical photogenerated carrier density of $\sim 10^{15}$ – 10^{16} cm^{-3} under 1-sun illumination.⁴⁸ Still, these perovskite solar cells show remarkable efficiencies under low-intensity indoor/solar illumination (trap-dominated regime) because of the defect-tolerant nature of the LHPs or the entirely different charge trapping/de-trapping mechanism in these materials compared to other PV materials.⁴⁹

In the case of Pb-free PIMs, the reported trap density is even higher than that of the halide Pb-based perovskites. Ran *et al.*⁵⁰ and Ivaturi *et al.*²³ reported trap densities of 10^{18} – 10^{17} cm^{-3} for PIM-based films, which are at least one-to-two orders of magnitude higher than those of the Pb-based halide perovskites. The devices with lower trap density showed a higher V_{OC} of 0.8 V under 1-sun illumination. To achieve a high V_{OC} (>1 V) for PIM-based IPVs, one good starting point would be to obtain high V_{OC} under 1-Sun and reduce the voltage losses under indoor lighting conditions. Thus, to maximise the V_{OC} of PIM-based indoor photovoltaics, there should be more investigation to explore the nature and energy of the traps (shallow, or deep), their density distribution as a function of composition, the formation energy required, and the feasible trap reduction methodologies. Fig. 3, adapted from reference⁵¹ shows how reducing the trap density can still retain a high V_{OC} even at low illumination intensities.

However, it is interesting to note that the V_{OC} losses for the best-performing CABI-Sb ($\text{PCE}(\text{i}) = 9.5\%$) and CsMAFA-Sb ($\text{PCE}(\text{i}) = 6.4\%$) PIM-based IPV devices are 0.13 V and 0.20 V, respectively when the illumination source changes from 1-Sun to 1000 lux WLED.^{26,31} Modest V_{OC} losses of ≈ 0.2 V have been reported even for high-performing IPVs.^{52,53} This suggests that V_{OC} losses due to lowering the light intensity are not very high in the IPV devices of these two materials. However, the low indoor V_{OC} values of just ~ 0.6 V in these devices are due to already low V_{OC} values achieved under 1-Sun, particularly in the case of CABI.^{24–26,28} Hoyer and co-workers examined the performance limiting factors of $\text{Cs}_2\text{Ag}(\text{Sb}_x\text{Bi}_{1-x})\text{Br}_6$ solar



Fig. 2 Optical bandgap, experimentally obtained V_{OC} , and voltage losses of PIM-based IPVs.



Fig. 3 The simulated graph showing how reducing the leakage current can sustain high photovoltage even under low intensity illumination (adapted from¹⁰⁵).



cells.⁵⁴ They demonstrated that sub-band gap states are accountable for the V_{OC} losses. Similarly, sub-band gap states are detected in CABI;¹⁸ however, their influence on CABI devices is not yet studied. On the other hand, density functional theory calculations have suggested that Sb-alloying in CABI increases the defect or vacancy formation energy.²⁶ While the co-alloying has nearly doubled the J_{SC} of the CABI IPV devices, it only resulted in very small enhancement in their V_{OC} values. The low V_{OC} values of the devices despite the suppressed intrinsic defect formation and carrier-self trapping could be explained by the non-radiative recombination of the charge carriers at the surface (interfacial recombination) or the grain boundaries (within the bulk) of the CABI layer. Such undesired recombination process may be promoted by the typical sub optimal morphology of CABI,^{18,24} which has been so far only partially addressed through additive and compositional engineering strategies.^{24,26} Therefore, morphological engineering and surface passivation strategies should be employed, inspired by works on both LHPs⁵⁵ and other PIMs,^{56–58} to mitigate the V_{OC} losses arising from SRH and interface recombination and push their PCE(s) towards their theoretical limits of 50–60% (see Fig. 1a). The low V_{OC} values also call for exploring different hole transport and electron transport layers (HTLs and ETLs) than those typically used in LHP-based devices (e.g., Spiro-OMeTAD and P3HT as HTLs; titanium and tin oxides as ETLs), as a good energy level matching is also crucial to achieving high V_{OC} .

Device operational stability needs immediate attention

Lead-free PIM films are usually stable when stored in air owing to the stable oxidation states of Bi^{3+} and Sb^{3+} . For instance, the X-ray diffraction (XRD) patterns of CABI and Sb-PIM collected before and after months of air storage show no changes (see Fig. 4a), indicating their high phase stability. In another study, CABI and AgBiI_4 stored in the air displayed no signs of degradation after exposure to solar light for one week.¹⁸ However, long-term stability of corresponding IPV cells is compulsory for their commercial applications. The stability of the photovoltaic cells is expected to be longer under indoor illumination than 1-Sun due to mild operation conditions, such as low-light intensity and no drastic variations in the humidity and light intensity. Commonly, the reported stability of LHP IPV cells has been assessed in terms of shelf-lifetime trends. For instance, Cheng *et al.* demonstrated the long-term stability of triple-anion methylammonium LHP cells with nearly 95% of their original PCE value retained after 2000 h of storage under indoor light.⁴⁰ Chen *et al.* reported the longest known shelf-life stability for LHP IPV cells based on a vacuum-deposited LHP layer, which shows a negligible loss in efficiency under continuous exposure to indoor light of intensities between 200 and 1000 lux for 16 months.⁵⁹ On the contrary, such long-term stability studies have not been yet reported for PIM-based IPV cells. In addition, to mimic the real-world behavior of the IPV cells,

their operational stability should be carefully examined, similarly to the case of LHP solar cells.⁶⁰ Among the available standard protocols to assess the operational stability of halide perovskite photovoltaics, maximum power point tracking (MPPT), which monitors the device performance under constant electric load and continuous illumination, sheds light on the intrinsic stability of the devices.⁶¹ As a case study, we report the data related to IPV devices employing CABI or triple-cation Sb-based PIM (CsMAFA-Sb). The performance of the unencapsulated devices in air ($\text{RH} \approx 50\%$) is monitored at the maximum power point (MPP) under continuous WLED (1000 lux) illumination (see Fig. 4b and c). The CABI IPV cell retains nearly 50% of its original PCE after 120 h of continuous operation. On the other hand, the CsMAFA-Sb device loses 40% of its original PCE already after 7 hours of air exposure. The operational stability of both CABI and CsMAFA-Sb IPV devices is poor,⁶² which leaves them still far from any practical utilization. This is in contrast with the respectable shelf-lifetime stability of CABI and CsMAFA-Sb films in the air (Fig. 4a).^{20,24} These observations exemplify that absorber material stability does not guarantee the corresponding device stability. In addition, the CABI device degrades more rapidly under 1-Sun (Fig. 4d) compared to the WLED illumination. This hints at the accelerated degradation of the device under high-light intensity illumination.

The degradation mechanisms of the photovoltaic devices of LHPs under 1-Sun illumination are widely studied and quite well-established.⁶⁰ One of the common degradation mechanisms in the LHP devices, as far as the absorber layer is concerned, is the ion migration under electric bias and illumination.^{60,63} Recently, Kulkarni *et al.* demonstrated that vacancy or defect-induced ion migration is a major degradation pathway of the Ag-Bi-I PIM-based solar cells under ambient storage.⁶⁴ This could be a plausible degradation pathway in many wide-bandgap PIMs as they often comprise a large number of defects.⁶⁵ However, further research should be performed to understand the underlying causes of the degradation in PIM-based photovoltaic cells under 1-Sun and indoor illuminations. In addition, effective strategies should be applied to extend the device lifetime of PIMs. Li *et al.* summarized the literature on various efficient strategies, which involve charged defect passivation, compositional tuning, surface passivation by organic and inorganic layers, and so on, to improve the operational stability of the LHP solar cells.⁶⁰ Although the optoelectronic behaviour of PIMs differs from LHPs, a good starting point may be to explore some of the strategies mentioned by Li *et al.*, which may also improve the V_{OC} values and other device parameters.

Prospect IPV absorbers

To address the above-mentioned instability and toxicity concerns of LHPs, the development of novel, and inherently more stable, PIMs has been the focus of recent research. Yet, more efforts are required to expand the library of potential non-toxic IPV absorbers. The following PIM candidates for IPV devices are proposed based on (i) suitability of band gaps (1.9–2.0 eV) for





Fig. 4 (a) XRD patterns of fresh and aged CABI films stored in air (reproduced from²⁴) and fresh and aged CsMAFA-Sb films stored in dry air (RH of 15%) (reproduced from³¹). MPP tracking of unencapsulated devices (in their n-i-p planar device architecture) of (b) CABI and (c) CsMAFA-Sb under WLED (1000 lux) illumination, and (d) CABI under 1-Sun illumination in air (RH ~50%).

indoor light-harvesting, (ii) reasonable PCEs under 1-Sun, (iii) optoelectronic properties suitable for photovoltaic applications, (iv) high defect-tolerance, and (v) air-stability.

Three-dimensional (3D) materials

Cesium germanium iodide (CsGeI_3), with a band gap of ~ 1.89 eV, has been explored for solar cell applications, yielding a PCE of 4.94%. This is one of the most efficient photovoltaic absorbers among the Pb-free perovskite structures.⁶⁶ Ba_2AgIO_6 , a low-temperature processable oxide analogue of halide perovskites, is another stable and encouraging alternative with a band gap (1.9 eV) close to the ideal value required for IPV absorbers.⁶⁷

3D MASbSI_2 (band gap = 2.03 eV) was recently found suitable for photovoltaic applications (PCE = 3.08%).⁶⁸

Two-dimensional (2D) materials

$\text{PEA}_2(\text{Ge/Sn})\text{I}_4$ possesses a band gaps around 2.1–2.2 eV.^{69,70} These are the candidates with the highest PCEs under 1-Sun when considering wide band gap materials ideal for IPV applications. For example, $(\text{PEA})_2\text{GeI}_4$ exhibits luminescence at room temperature with a moderate lifetime, showing promise for photovoltaic applications. Another popular family of compounds, $\text{A}_3(\text{Sb/Bi})_2\text{X}_9$, with bandgaps in the 1.9–2.1 eV range is also not much explored for IPV applications and can be a great prospect considering their favourable optoelectronic properties.^{71–74} Among these, $\text{MA}_3\text{Sb}_2\text{I}_{9-x}\text{Cl}_x$ (band gap = 2.2 eV) yielded a PCE of 3.34% under 1-Sun,⁷⁵ which makes it a

potential IPV absorber. Sb–Bi co-alloying in these materials may favourably modify their optoelectronic properties, as in the case of CABI. Other 2D candidates for consideration can be MA_2PdCl_4 (band gap = 2.2 eV) and $\text{CsBi}_3\text{I}_{10}$ (band gap = 1.8 eV).⁷⁶

Double perovskites and vacancy-ordered double perovskites, $\text{A}_2\text{Ag}(\text{Sb/Bi})\text{X}_6$ (A = Cs and MA; X = Br and Cl), having bandgap tunability over a wide range (1.6–2.6 eV), offer great potential as candidates that remain unexplored for IPV applications.^{77–82} The double perovskite $\text{Cs}_2\text{AgBiBr}_6$, with a PCE of 2.8% and bandgap around 2.2 eV, is the most explored PIM when it comes to solar cells.⁸³ Additionally, the high air-stability and the earth abundant nature of the involved elements make $\text{Cs}_2\text{AgBiBr}_6$ ideal candidates for IPV applications. Cs_2TiBr_6 (band gap = 1.8 eV), a vacancy-double perovskite with a reported PCE (1-Sun) of $\approx 3.3\%$, is also a potential IPV absorber.^{84,85} Cs_2PdX_6 , with tunable band gaps over the 1.6–2.22 eV range by halide compositional engineering, are suitable for different indoor light environments.^{86,87}

Although the IPV performance of a silver iodobismuthate with the composition of AgBiI_4 has been already examined,²¹ another member of the same family, Ag_3BiI_6 that yielded PCE values up to 4.2–5.4% (and notable J_{SC} and FF) under 1-Sun due to improved charge transport⁸⁸ may ensure $>10\%$ IPV efficiencies. Antimony sulfide (SbSI) with a band gap of ≈ 2.2 eV, high defect-tolerance (dielectric constant in the order of 10^4), and high stability offers a great promise for IPV applications.⁸⁹ The IPV performance of BiOI , a deep-trap tolerant,⁹⁰ can be further improved if the morphology-related limitations are addressed.⁹¹



In conclusion, PIMs have had a promising start for IPVVs. Their low V_{OC} values of $\sim 0.5\text{--}0.6$ V remain the major drawback restricting them from reaching PCE(i) values beyond 10% and towards their theoretical limits. The wide band gap nature and typical sub optimal morphology of PIMs typically lead to

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