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Recent progress in layered metal halide perovskites for solar cells, photodetectors, and field-effect transistors

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Metal halide perovskite materials demonstrate immense potential for photovoltaic and electronic applications. In particular, two-dimensional (2D) layered metal halide perovskites have advantages over their 3D counterparts in optoelectronic applications due to their outstanding stability, structural flexibility with a tunable bandgap, and electronic confinement effect. This review article first analyzes the crystallography of different 2D perovskite phases [the Ruddlesden–Popper (RP) phase, the Dion–Jacobson (DJ) phase, and the alternating cations in the interlayer space (ACI) phase] at the molecular level and compares their common electronic properties, such as out-of-plane conductivity, crucial to vertical devices. This paper then critically reviews the recent development of optoelectronic devices, namely solar cells, photodetectors and field effect transistors, based on layered 2D perovskite materials and points out their limitations and potential compared to their 3D counterparts. It also identifies the important application-specific future research directions for different optoelectronic devices providing a comprehensive view guiding new research directions in this field.

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1. Introduction

Metal halide perovskites are highly versatile semiconducting materials due to their long charge carrier lifetime, high light absorption coefficient, and narrow emission bandwidth.^{1–7} They have attracted significant research attention worldwide in materials science, physics, and chemistry. In 2009, Kojima *et al.* first demonstrated a solar cell using a metal halide perovskite as an active layer producing a power conversion efficiency (PCE) of ~3.8%.⁸ Incredible performance improvement in halide perovskite solar cells has since been achieved reaching a certified PCE of 25.7% in 2022.⁹ Moreover, metal halide perovskites have immense potential for various optoelectronic devices, such as light-emitting diodes, field-effect transistors, and photodetectors, due to their excellent optical and electronic properties.^{10–14} Three-dimensional (3D) perovskites have been extensively studied with an empirical formula of ABX_3 (Fig. 1) and a crystal structure with the corner-sharing six-coordinated octahedra, where A is monovalent cations (Cs^+ , Rb^+ , $MA^+ = (CH_3NH_3)^+$, or $FA^+ = (CH(NH_2)_2)^+$), B is divalent metal cations (Pb^{2+} or Sn^{2+}), and X is halide anions (Cl^- , Br^- , or I^-). The probable crystallography can be deduced by the Goldschmidt factor (t) on whether a 3D or 2D perovskite structure is formed.^{6,15} t is defined as the ratio of the distance

between A–X and B–X according to the idealized solid-sphere model ($t = (R_A + R_X) / \sqrt{2}(R_B + R_X)$), where R_A , R_B , and R_X are the corresponding effective ionic radii. Typically, a 3D perovskite has a Goldschmidt factor in the range of 0.81 to 1.11, whereas a 2D perovskite would have a value higher than 1.11. The ABX_3

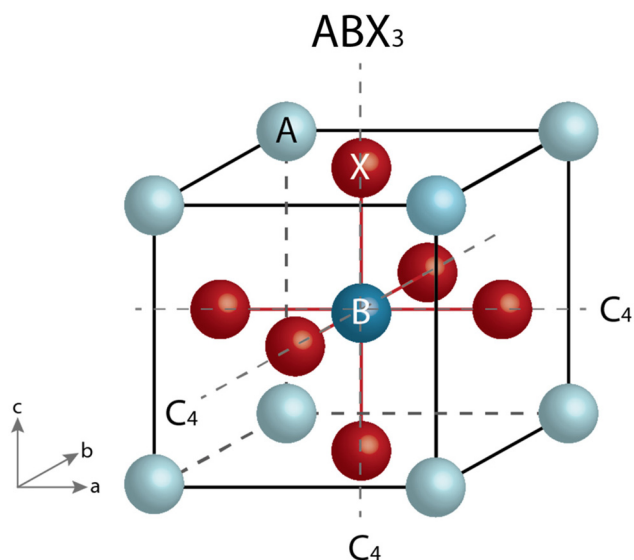


Fig. 1 The perovskite crystal structure with the molecular formula of ABX_3 (A: Cs^+ , Rb^+ , $MA^+ = (CH_3NH_3)^+$, or $FA^+ = (CH(NH_2)_2)^+$; B: Pb^{2+} or Sn^{2+} ; and X: Cl^- , Br^- , or I^-).

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3D structure can contain a small organic cation at the A site. A large organic cation with a long carbon chain cannot be integrated into a 3D structure that forms a two-dimensional (2D) structure. The 2D perovskite can be imaged by slicing the 3D structure along the crystallographic plane, forming sheets, and inserting the halide anions at the $[BX_6]^{2-}$ octahedra corner to satisfy the centre metal coordination and then adding the large cation as a spacer between the inorganic sheets. The cleaving can be done along three different planes of the 3D structure to establish the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ oriented 2D perovskites. Notably, this molecular-level dimension reduction differs at the morphology level, in which the framework remains the same but the crystallite size changes. At the morphology level, the system shows size-dependent properties at the nanoscale. For instance, as the morphology changes, MAPbI₃ results in a 3D nanocube, a 2D nanoplate, and a 1D nanowire. Importantly, all of them are 3D materials in solid-state definition with the molecular formula of ABX₃ and limited candidates due to the same framework. Therefore, molecular-level 2D metal halide perovskites demonstrate various kinds of spacers and come with a tunable bandgap, unique structure confinement properties, and long stability. This review will focus on molecular-level 2D metal halide perovskites with different crystallographic phases for different types of semiconducting applications.

2. Low-dimensional layered metal halide perovskites

More than 700 types of 2D metal (Pb or Sn) halide perovskites have been reported to date, demonstrating a remarkable struc-

tural diversity and tunable optoelectronic properties by different thicknesses, cage cations, and spacer cations.^{16,17} They can be classified into three categories: the Ruddlesden–Popper (RP)¹⁸ phase, the Dion–Jacobson (DJ)¹⁹ phase, and the alternating cations in the interlayer space (ACI)²⁰ phase as shown in Fig. 2 with the general formulae of $A_2A'_{n-1}B_nX_{3n+1}$, $AA'_{n-1}B_nX_{3n+1}$, and $AA'_nB_nX_{3n+1}$, respectively.

2.1 Ruddlesden–Popper (RP) phase perovskites

The most common layered metal halide perovskites are based on the RP structure with long monoammonium chains. The general formula is $A_2A'_{n-1}B_nX_{3n+1}$, in which the A cation is the long carbon chain spacer and the A' cation is the small cation (MA^+ , FA^+ , or Cs^+). They usually interdigitate between the $[BX_6]^{2-}$ inorganic stack and present a large separation, also known as *d* spacing (indicated in Fig. 2) albeit insulating. The inorganic layers in the RP phase structure are offset by one octahedral unit with $(1/2, 1/2)$ displacement through the *ab*-plane. Therefore, inorganic layers slide in a staggered composition in which the $[BX_6]^{2-}$ octahedral unit is not perfectly stacked on top of one another. Due to this, the spatial confinements of the charge carrier and the dielectric contrast between the inorganic stack and the organic spacer increase resulting in a high exciton binding energy around 150 to 500 meV, typically ten times larger than those of 3D perovskites (10–50 meV).²²

In 1994, Mitzi *et al.* reported the first homologous series of linear carbon chain cation 2D perovskites $(C_4N_9NH_3)_2(MA)_{n-1}Sn_nI_{3n+1}$ ($n = 1-5$) and their intrinsic electronic properties.²³ The Hall carrier concentration was estimated to be $7 \times 10^{18} \text{ cm}^{-3}$ with a low resistivity of $\sim 10^{-2} \Omega \text{ cm}$ for the $n = 5$ compound. These values set up 2D metal halide

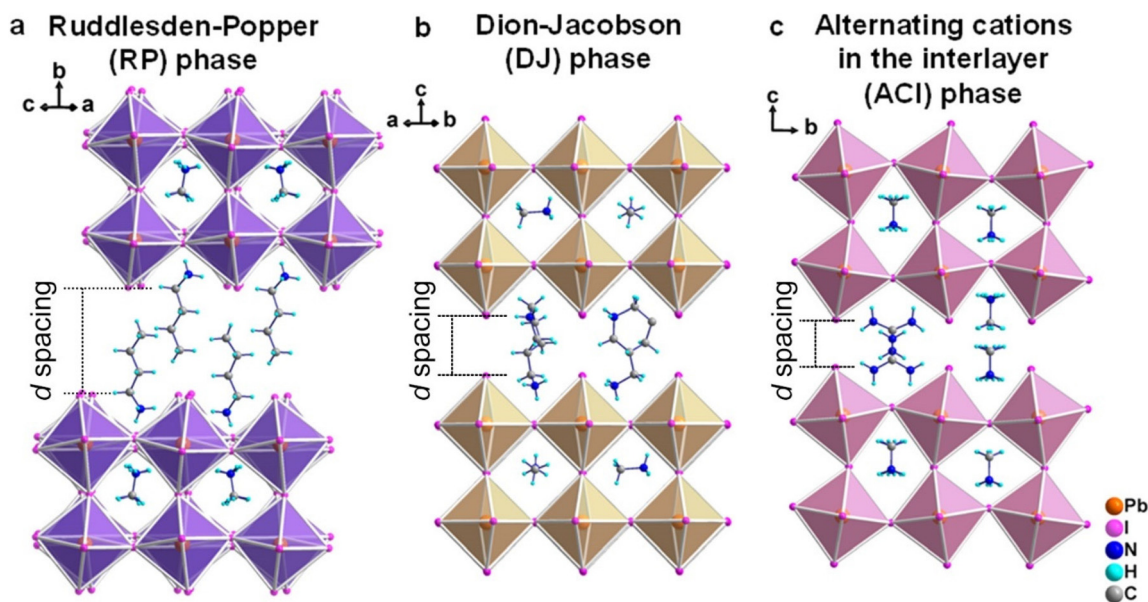


Fig. 2 Lower dimensional layered perovskite structures. (a) The Ruddlesden–Popper (RP) phase, (b) the Dion–Jacobson (DJ) phase, and (c) the alternating cations in the interlayer space (ACI) phase.²¹

small separation between the $[\text{Pb}(\text{SCN})_2\text{Br}_2]^{2-}$ inorganic slab, the single crystal demonstrates a relatively low exciton binding energy (160 meV) compared to other A-site substituted layered perovskites (>200 meV), as shown in Fig. 3e.

2.2 Dion–Jacobson (DJ) phase perovskites

DJ phase perovskites typically incorporate diammonium organic cations as a spacer—different from RP phase perovskites. The molecular formula is $\text{AA}'_{n-1}\text{B}_n\text{X}_{3n+1}$ (A cation: diammonium organic cation, A' cation: MA^+ , FA^+ , or Cs^+). Intriguingly, the diammonium cation can form electrostatic interaction at two separate sites (Fig. 2b), resulting in narrow separation, thus significantly limiting the transport energy barrier. In DJ phase oxide perovskites, for example, a large cation spacer corresponds to (0, 0) no shift ($P4/mmm$ space group) through the ab -plane in a unit cell, and a small cation spacer relates to the (1/2, 0) shift ($I4/mmm$ space group).²⁰ However, a layered hybrid halide perovskite should have more than one cation site in the interlayer per formula unit. Therefore, the DJ phase may be more appropriately referred to as a “perovskite-like” phase.³⁵ In 2018, Mao *et al.* reported the first homologous 3-aminomethylpiperidinium (3AMP) and 4-aminomethylpiperidinium (4AMP) series of DJ phase perovskites from $n = 1$ to 4 with the general molecular formula of $\text{AA}'_{n-1}\text{B}_n\text{X}_{3n+1}$.¹⁹ In 2019, the same group successfully synthesized a thick (4AMP) $\text{MA}_6\text{Pb}_7\text{I}_{22}$ single crystal with seven layers (Fig. 4a).³⁶ They discovered that the DJ phase perovskite

has less lattice strain which causes a broader electronic band and lower bandgap energy than RP phase perovskites. In terms of thermodynamic stability, which has an implication on its extrinsic stability, some argued that the DJ phase is less stable than the RP phase.³⁷ However, Shang and co-workers used the DFT computation to show that the arene-based DJ phase has a higher dissociate energy and better kinetic stability than the RP phase.³⁸ Indeed, various works reported enhanced optical and humidity stabilities as the alkyl chain length increases in arene-based DJ phase perovskites^{39–43} offering opportunities for the use of the DJ phase for optoelectronic applications.

The interlayer distance in layered halide perovskites has significant implications for the quantum and dielectric confinement effect.⁴⁴ In 2018, Ma and colleagues used a short propane-1,3-diammonium (PDA) cation to synthesize a (PDA) $\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 2–4$) series layered perovskite.⁴⁵ It demonstrated the shortest interlayer distance of 2 Å in DJ phase perovskites. Huang and coauthors used transient photoluminescence mapping to visualize that the DJ phase perovskite not only confines the charge carrier in the in-plane direction but also becomes more conductive than the RP phase in the out-of-plane direction (Fig. 4b).⁴⁶ Thus, the DJ phase perovskite provides an expansive playground for more extensive photovoltaic and electronic application studies. While examples given in this section are mainly MA-based layered perovskites,²⁶ similar principles can be applied to FA-based DJ phase perovskites.

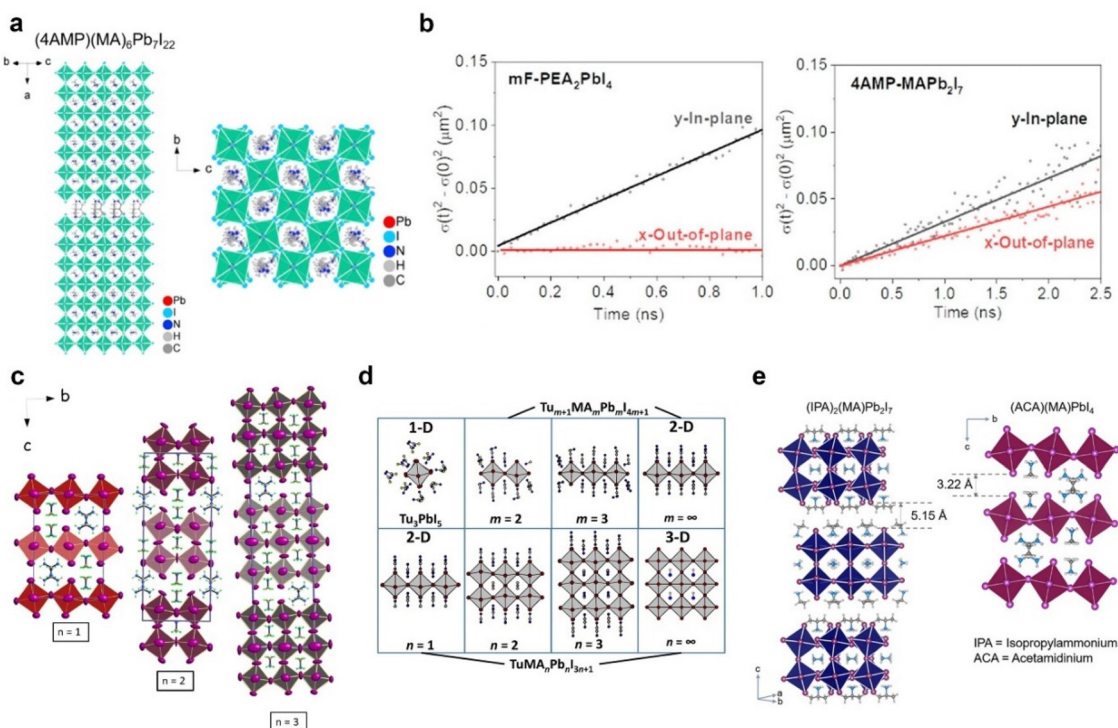


Fig. 4 Illustrations of some Dion–Jacobson (DJ) phase perovskites reported. (a) The crystal of (4AMP) $\text{MA}_6\text{Pb}_7\text{I}_{22}$ from the top-down and side views.³⁶ (b) Time-dependent mean-square distribution for photoluminescence emission spot broadening of RP and DJ phase perovskites along the in-plane and out-of-plane directions.⁴⁶ (c) Crystal structure of (GA)(MA) $n\text{Pb}_n\text{I}_{3n+1}$ ($n = 1–3$).²⁰ (d) Overview of the crystal structure of the TuI/MAI/ PbI_2 system.⁴⁹ (e) Crystal structure of (IPA)(MA) Pb_2I_7 and (ACA)(MA) PbI_4 .⁵⁰

2.3 Alternating cations in the interlayer space (ACI) phase perovskites

The ACI phase combines the RP phase's chemical formation and the DJ phase's structural feature with the general formula of $AA'_nB_nX_{3n+1}$. The A-site cations include a small monocation (A' cation: Cs^+ , MA^+ , or FA^+) inside the perovskite cage and between the inorganic stacks alternating with a triammonium or diammonium cation (A cation) as spacers (Fig. 2c). The particular order leads to doubling of the unit cell along with the b -axis resulting in an ideal undistorted cell. The inorganic layers demonstrate a $(1/2, 0)$ offset along the ab plane, similar to the DJ phase perovskite. However, the interlayer sites differ from the DJ phase perovskite according to the charge balance restriction resulting in different centering of the unit cells. In 2017, Soe and colleagues used guanidinium (GA) to fabricate the first series of ACI phase $(\text{GA})(\text{MA})_n\text{Pb}_n\text{I}_{3n+1}$ ($n = 1-3$) perovskite single crystals (Fig. 4c).²⁰ The optical property measurement of the $(\text{GA})(\text{MA})_n\text{Pb}_n\text{I}_{3n+1}$ series shows a lower bandgap than that of the similar structure $\text{BA}_n\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ RP phase perovskites due to their smaller crystallographic distortion. Moreover, the $n = 3$ compound when applied as an active layer in a solar cell yielded a PCE of 7.3%. In 2019, Luo *et al.* used $(\text{GA})(\text{MA})_3\text{Pb}_3\text{I}_{10}$ as an active layer for solar cell demonstration, yielding a PCE of 18.5%.⁴⁷ Three years later, Zhang and colleagues used $(\text{GA})(\text{MA})_5\text{Pb}_5\text{I}_{16}$ to fabricate a highly efficient layered perovskite solar cell with a PCE of 22.3%.⁴⁸ In 2021, Daub *et al.* reported an analogous layered perovskite by using protonated thiourea (Tu^+) to synthesize $(\text{Tu})(\text{MA})\text{PbI}_4$ single crystals.⁴⁹ Its detailed crystal structure transition from 1D to 3D can be controlled by the chemical composition ratio (Fig. 4d). Recently, Mao and coworkers reported the ACI phase acetamidinium (ACA) perovskite single crystal, $(\text{ACA})(\text{MA})\text{PbI}_4$.⁵⁰ The interlayer distance is about 3.22 Å, which is more compact than that of the $(\text{IPA})(\text{MA})\text{Pb}_2\text{I}_7$ (separation distance of 5.15 Å) RP phase perovskite (Fig. 4e). As the separation distance decreased, the out-of-plane exciton transportation was improved, boosting the performance of the solar cell when the material was used. Zhu *et al.* reported two different chiral-polar hybrid ACI phase perovskite single crystals, $(\text{MPA})(\text{EA})\text{PbBr}_4$ ⁵¹ and $(\text{PPA})(\text{EA})\text{PbCl}_4$.⁵² Surprisingly, these two kinds of perovskites demonstrated self-powered circularly polarized light detection with high detectivity. It was the first realization of the chiral-polar photovoltaic effect in ACI phase perovskites. Even though ACI phase perovskites have been used in demonstrating solar cell devices, they were seldom applied in other semiconductor devices, such as light-emitting diodes or field-effect transistors possibly due to the limited diversity of ACI phase perovskites. Therefore, multiple research avenues exist to explore further new ACI phase perovskites and new properties for various semiconductor device applications.

3. Layered perovskite applications

There is an immense opportunity to apply layered metal halide perovskites for various semiconducting device applications. In

2021, the markets for solar cells, photodetectors, and field-effect transistors were worth around USD 91.6 billion, with a compound annual growth rate of 5–8%. Moreover, perovskite devices can be fabricated *via* a facile, solution-processed route, presenting potential upscaling advantages. In particular, the various crystallographic phases of layered metal halide perovskites (RP, DJ, and ACI phases) can be tailored for different device geometry designs. For example, DJ and ACI phase perovskites have lower exciton binding energy than the RP phase enabling vertical charge transport and are therefore more suitable for devices such as solar cells. On the other hand, RP phase perovskites present a better quantum confinement effect thus improving horizontal charge transport, making them more suitable than the other phases for planar geometry devices, such as field-effect transistors. This section will discuss the demonstrated applications of layered perovskites in optoelectronic devices.

3.1 Solar cell

While organic–inorganic hybrid perovskite solar cells are promising emerging thin film photovoltaic technology,⁵³ they are sensitive to moisture and heat, thus hindering their applications.⁵⁴ For example, a small amount of a Lewis base, such as water (from rain and humid air), can disrupt the hydrogen bond, coordinate with metal cations, and dissolve the perovskite material in 3D perovskites, along with other phase-induced changes causing degradation. As the water-induced decomposition process readily occurs due to the presence of volatile small organic cations, such as MA^+ and FA^+ in the A-site weakening non-covalent bonds between the organic and inorganic framework,⁵⁵ replacing these small and unstable hygroscopic organic cations with bulkier hydrophobic organic cations in the perovskite absorber layer in a solar device can improve its ambient stability. The absorber will inevitably be a lower-dimensional layered perovskite as the introduction of bulkier organic cations distorts the perovskite framework. Great progress has been made in layered perovskite solar cells with the PCE rapidly improving from 4.7% to 22.3% within only eight years (Fig. 5a).^{47,48,56–61} Notable demonstrations including device structure and performance are listed in Table 1.

In 2014, Smith *et al.* demonstrated the first RP phase layered perovskite solar cells using $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ ($\text{PEA}^+ = \text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3^+$).⁵⁶ The PCE was relatively low (4.7%) then, but the device demonstrated better moisture resistance than the control MAPbI_3 device. The relatively poor efficiency is due to the inhibition of vertical charge transport through the organic cation, which acted as an insulator between the conducting inorganic layers. In 2016, Tsai and colleagues overcame this issue by producing a near-single crystalline quality $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ ($\text{BA}^+ = \text{CH}_3(\text{CH}_2)_3\text{NH}_3^+$) thin film for a solar device producing a PCE of 12.5%. The un-encapsulated device also retained 60% of its initial PCE after 2250 hours of AM1.5G illumination with a relative humidity (RH) of 65%.⁵⁷ This breakthrough revived the interest in layered perovskite solar cells. Subsequently, Fu and co-authors introduced NH_4SCN and NH_4Cl additives into the $(\text{PEA})_2\text{MA}_4\text{Pb}_5\text{I}_{16}$

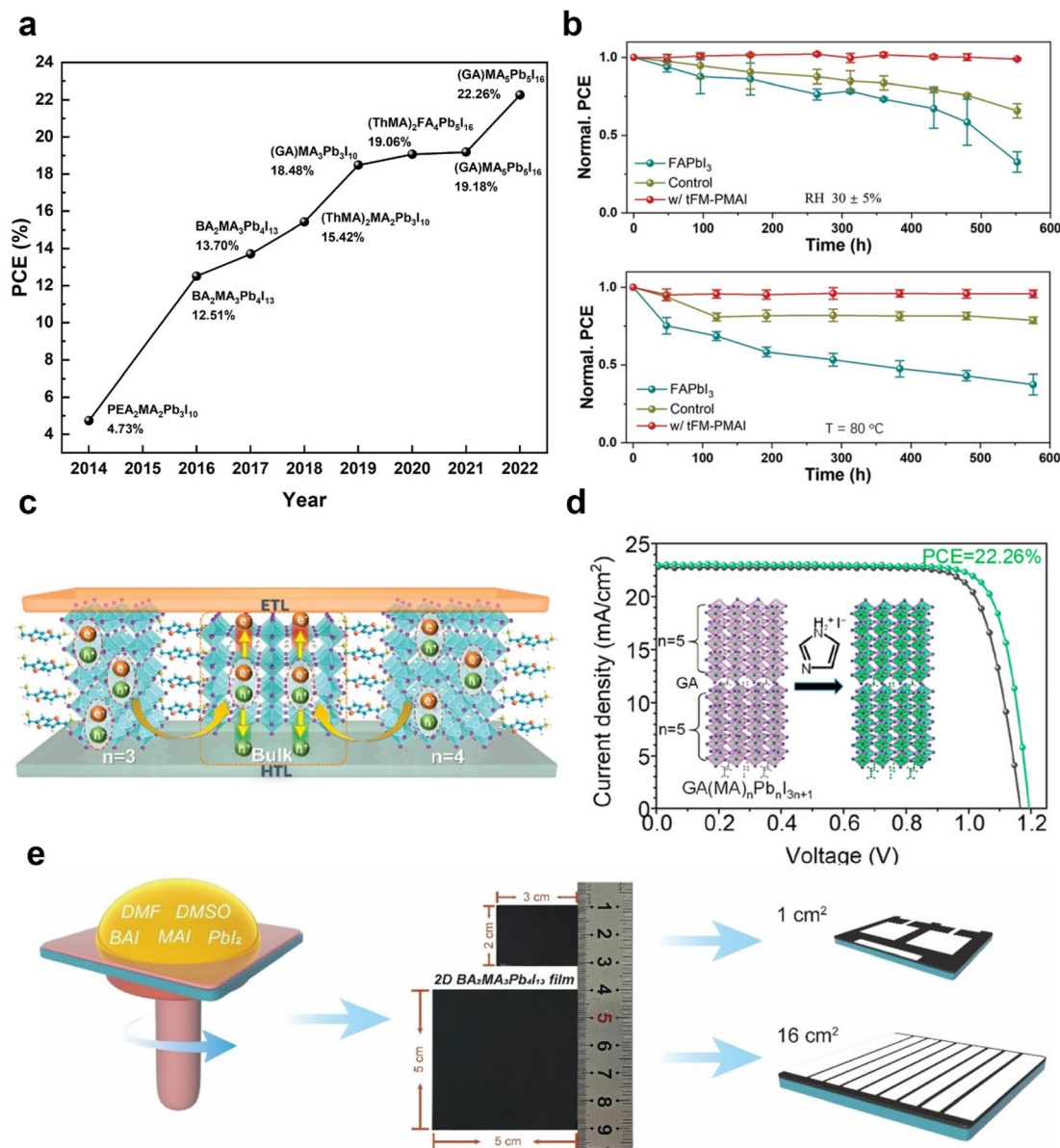


Fig. 5 Application of layered perovskites for photovoltaics. (a) PCE of notable layered perovskite solar cells from 2014 to 2022.^{47,48,56–61} (b) Ambient and thermal stability measurements of a (ThMA)₂FA₄Pb₅I₁₆ perovskite solar cell.⁶⁰ (c) Illustration of the charge transfer of (TTDMA)MA_{n-1}Pb_nI_{3n+1} film.⁶⁸ (d) Reverse and forward scanned J–V curves of Iml post-treated (GA)(MA)₅Pb₅I₁₆ perovskite solar cells with a PCE of 22.3%.⁴⁸ (e) Schematic diagram of a mini-module (5 × 5 cm²) based on BA₂MA₃Pb₄I₁₃ perovskite solar cells.⁶⁹

layered perovskite demonstrating a solar device with a best PCE of 14.1%.⁶² The NH₄SCN additive was found to regulate the perovskite grain orientation enhancing crystallinity while the NH₄Cl additive passivated the interfacial traps between the electron transport layer and the perovskite layer.

In terms of layered perovskite crystallography, structural ordering of cation spacers can be induced by fluorine substitution in an aromatic cation spacer, such as PEA.⁶³ Zhang *et al.* used a *para*-position-fluorine-substituted PEA (F-PEA) to fabricate (F-PEA)₂MA₂Pb₅I₁₆ layered perovskite solar cells,⁶⁴ thus improving the best PCE from 9.7% to 13.6% after fluoride substitution due to the enhanced lifetime and lower trap

density of the perovskite layer. Furthermore, an un-encapsulated (F-PEA)₂MA₂Pb₅I₁₆ device maintained 65% of its initial PCE after 576 h at 70 °C. In the future, it may be possible to include the use of perfluoroarene-based cations⁶⁵ and their 1 : 1 mixtures with arene spacers (which went as far back as in 2003)⁶⁶ applicable to the DJ phase⁶⁷ for controlling the crystallographic characteristics and their associated properties for solar cell demonstrations.

In 2018, Lai and colleagues used 2-thiophenemethylammonium (ThMA) cations as a spacer for (ThMA)₂MA₂Pb₃I₁₀ solar cell demonstration,⁵⁹ resulting in a PCE of 15.4% using the MAI assisted-film forming technique. Two years later, the same

Table 1 Performance layered perovskite solar cells

Materials	Device configuration	PCE (%)	PCE remained ratio (%)	RH (%)	Conditions	Times	Year
RP phase perovskites							
PEA ₂ MA ₃ Pb ₄ I ₁₃ ^a	FTO/PEDOT:PSS/perovskite/C ₆₀ /BCP/Ag ⁷⁰	18.5	90	40	Ambient	1200 h	2020
(F-PEA) ₂ MA ₂ Pb ₅ I ₁₆ ^a	FTO/c-TiO ₂ /perovskite/spiro-OMeTAD/Au ⁶⁴	13.6	65	N/A	Ambient, 70 °C	576 h	2019
(F-PEA) _{0.8} GA _{0.2}) ₂ MA ₃ Pb ₄ I ₁₃ ^a	ITO/PTAA/perovskite/C ₆₀ /BCP/Cu ⁷¹	17.5	87	40–50	Ambient	500 h	2022
BA ₂ MA ₃ Pb ₄ I ₁₃ ^a	ITO/SnO ₂ /perovskite/spiro-OMeTAD/MoO ₃ /Au ⁷²	16.3	93.8	65 ± 10	Ambient	4680 h	2021
BA ₂ MA ₄ Pb ₅ I ₁₆	ITO/PTAA/perovskite/C ₆₀ /BCP/Ag ⁷³	17.7	96.7	—	N ₂	1000 h	2022
BA ₂ MA ₃ Pb ₄ I ₁₃ ^a	ITO/P3CT-BA/perovskite/PCBM/BCP/Ag ⁶⁹	17.6	90	40–50	Ambient, 20 °C	2400 h	2022
(PA) ₂ MA ₄ Pb ₅ I ₁₆ ^a	FTO/TiO ₂ /perovskite/spiro-OMeTAD/Au ⁷⁴	10.4	98	60	Ambient, 25 °C	500 h	2018
(ThMA) ₂ MA ₂ Pb ₃ I ₁₀ ^a	ITO/PEDOT:PSS/perovskite/PCBM/BCP/Ag ⁵⁹	15.4	90	30 ± 10	N ₂	1000 h	2018
(ThMA) ₂ FA ₄ Pb ₅ I ₁₆ ^a	ITO/PEDOT:PSS/perovskite/PCBM/BCP/Ag ⁶⁰	19.1	99	30 ± 5	Ambient	552 h	2020
DJ phase perovskites							
(3AMP)MA ₃ Pb ₄ I ₁₃	ITO/PEDOT:PSS/perovskite/C ₆₀ /BCP/Ag ¹⁹	7.3	—	—	—	—	2018
(4AMP)MA ₃ Pb ₄ I ₁₃	ITO/PEDOT:PSS/perovskite/C ₆₀ /BCP/Ag ¹⁹	4.2	—	—	—	—	2018
(PDMA)FA ₂ Pb ₃ I ₁₀ ^a	FTO/c-TiO ₂ /m-TiO ₂ /perovskite/spiro-OMeTAD/Au ⁷⁵	6.9	85	30–50	Ambient	60 days	2018
(PDA)MA ₃ Pb ₄ I ₁₃ ^a	FTO/TiO ₂ /perovskite/spiro-OMeTAD/Au ⁷⁶	13.3	≥95	85	Ambient, 85 °C	168 h	2019
(BDA)(C _{80.1} FA _{0.9}) ₄ Pb ₅ I ₁₆ ^a	FTO/c-TiO ₂ /m-TiO ₂ /perovskite/spiro-OMeTAD/Au ⁷⁷	18.2	90	35	Ambient, 35 °C	800 h	2020
(TTDMA)MA ₃ Pb ₄ I ₁₃ ^a	ITO/PEDOT:PSS/perovskite/PCBM/BCP/Ag ⁶⁸	18.8	≥99	—	N ₂	4400 h	2021
ACI phase perovskites							
GAMA ₃ Pb ₃ I ₁₀ ^a	FTO/c-TiO ₂ /perovskite/PCBM/Ag ⁷⁸	14.1	88	30 ± 10	Ambient, 25 °C	240 days	2019
GAMA ₃ Pb ₃ I ₁₀ ^a	FTO/c-TiO ₂ /perovskite/PCBM/Ag ⁴⁷	18.5	95	30 ± 10	Ambient, 25 °C	131 days	2019
GAMA ₃ Pb ₅ I ₁₆ ^a	FTO/c-TiO ₂ /perovskite/spiro-OMeTAD/Au ⁶¹	19.2	95	30 ± 10	Ambient, 25 °C	123 days	2021
GAMA ₃ Pb ₅ I ₁₆	FTO/c-TiO ₂ /perovskite/spiro-OMeTAD/Au ⁴⁸	22.3	93.81	25	Ambient, 25 °C	50 days	2022

^a Device without encapsulation.

group substituted the MA⁺ cation with FA⁺ to fabricate (ThMA)₂FA₄Pb₅I₁₆ solar cells with a PCE of 19.1%⁶⁰ and the unencapsulated device retained 99% of its initial PCE after 552 h of storage in ambient environment (RH = 30 ± 5%) or 96% of its initial PCE after 576 h of thermal annealing at 80 °C in N₂, respectively.

Due to lower exciton binding energy for vertical charge transport, DJ and ACI phase perovskite cells have recently outperformed their RP phase counterparts. In 2021, Xu *et al.* designed and synthesized a new type of fused-thiophene-based spacer, thieno[3,2-*b*]thiophene-2,5-diylidimethanaminium iodide (TTDMAI), for DJ phase perovskite solar cells.⁶⁸ TTDMAI provides a long π -conjugation chain and increasing grain size with vertical orientation due to the solid molecular interaction with the template. Thus, the exciton dissociation and charge transport were enhanced, as illustrated in Fig. 5c. The outstanding (TTDMA)MA₃Pb₄I₁₃ solar cell demonstrated a PCE of 18.8%. In 2022, Zhang *et al.* reported that the ACI phase (GA)(MA)₅Pb₅I₁₆ perovskite solar cells and amphoteric imidazolium iodide (ImI) post-treatment of the perovskite layer were responsible for boosting the outstanding device PCE to 22.3% (Fig. 5d).⁴⁸

While large area solar cell demonstration using layered perovskites is still in its infancy at the time of writing of this review, in 2022, Han *et al.* reported the first 5 × 5 cm² layered perovskite solar cell mini-module (active area = 16 cm²) based on BA₂MA₃Pb₄I₁₃ perovskites (Fig. 5e).⁶⁹ The best module PCE reached 11.1%, while the average was 10.5%. To date, no scalable processes, such as roll-to-roll, blade coating, or spray coating, have been applied to layered perovskite solar cells for module fabrication. Thus, there are opportunities for large area cell or module demonstrations using high-performance and more stable layered perovskites.

3.2 Photodetector

Photodetectors absorb light at a particular wavelength (range) of interest, and convert it into an electrical signal. The figures of merit, responsivity (*R*) and detectivity (*D*^{*}) are vital parameters for evaluating the performance of a photodetector. Responsivity refers to the net photocurrent generated from the incident light absorbed by the device in a unit of time. Detectivity reflects the capacity limit of a photodetector to detect low-intensity light. Layered metal halide perovskites are tunable in terms of light absorption wavelength range by changing the [BX₆]⁴⁻ octahedra layer number between two adjacent spacers.²⁹ In addition, the inherent 2D quantum-confined structure in layered perovskites facilitates rapid photogenerated electron-hole pair dissociation which is more pronounced in RP-phase perovskites enabling rapid electron extraction to the inorganic conduction band with high carrier mobility reducing charge recombination and improving photoconductivity gains.⁷⁹ These unique properties of layered perovskites make them promising candidates for high-performance photodetectors. Some of the layered perovskite photodetectors reported are listed in Table 2.

In 2016, Zhou *et al.* demonstrated a BA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (BA⁺ = C₄H₉NH₃⁺) thin-film-based perovskite photodetector with *n* = 1–3.⁸⁰ The layered perovskite exhibits an *n*-dependent absorbance spectrum and band diagram. The photoresponse corresponds to the inner perovskite layer thickness. Thus, the best performance was observed for larger *n* devices (Fig. 6a). In particular, the responsivity under 3.0 mW cm⁻² white illumination for *n* = 1, 2, and 3 were 3.00, 7.31, and 12.78 mA W⁻¹, respectively. The relatively low responsivity was due to the presence of the insulating organic spacer acting as a charge barrier

Table 2 Performance of layered perovskite photodetectors

Materials	Morphology	Device fabrication	V_D (V)	R ($A W^{-1}$)	D^* , light source (Jones, nm)	t_r/t_d	Year ^[ref.]
RP phase perovskites							
$(BA)_2(MA)_2Pb_3Br_{10}$	Single crystal	STL	5	—	3.6×10^{10} , 420	150/570 μs	2017 ⁸⁹
$Cs_2PbI_2Cl_2$	Single crystal	Solid-state method	10	—	—	0.2/0.06 s	2018 ³³
$(PEA)_2PbBr_4$	Single crystal	Evaporation process	10	3.148×10^{-2}	1.55×10^{13} , 365	0.41/0.37 ms	2019 ⁹⁰
$(PA)_2(GA)Pb_2I_7$	Single crystal	STL	10	47	6.3×10^{12} , 550	0.94/2.18 ns	2019 ⁸³
$(BPA)_2PbBr_4$	Single crystal	STL	0	10^{-4}	10^7 , 377	27/30 μs	2020 ⁹¹
BDAPbI ₄	Single crystal	STL	10	9.27×10^{-1}	1.23×10^{11} , 462	187/163 μs	2020 ⁹²
$(BA)_2PbBr_4$	Single crystal film	AVC	4	4.5×10^{-2}	$\sim 1.02 \times 10^{12}$, 400	9.7/8.8 ms	2021 ⁹³
$Cs_2Pb(SCN)_2Br_2$	Single crystal	AVC	0.5	8.46×10^{-3}	1.2×10^{10} , 405	2.6/2.3 ms	2022 ³⁴
$(OA)_2(FA)_{n-1}Pb_nBr_{3n+1}$	Microplates	Drop-cast	9	32	—	0.25/1.45 ms	2017 ⁸²
$(BA)_2PbI_4$	Microplates	Solution-vapor method	5	—	—	58.8/56.6 ms	2018 ⁹⁴
$(PPA)_3Pb_2I_7$	Nanosheets	ASAC	—	—	1.2×10^{10} , 515	850/780 μs	2019 ⁹⁵
$(BA)_2(MA)_3Pb_4I_{13}$	Nanosheets	Inkjet-printed	40	0.17	3.7×10^{12} , 532	24/65 ms	2020 ⁹⁶
$(BA)_2(MA)Pb_2I_7$	Nanoplates	Drop-cast	10	4.5×10^{-3}	3.09×10^{10} , 550	<100 ms	2020 ⁹⁷
$(BA)_2(MA)_2Pb_3I_{10}$	Thin film	Spin coated	30	3×10^{-3}	—, white light	28.4/27.5 ms	2016 ⁸⁰
$(BA)_2(MA)Pb_2I_7$	Thin film	Spin coated	30	7.31×10^{-3}	—, white light	8.4/7.5 ms	2016 ⁸⁰
$(BA)_2PbI_4$	Thin film	Spin coated	30	1.278×10^{-2}	—, white light	10.0/7.5 ms	2016 ⁸⁰
$(BA)_2(MA)_3Pb_4I_{13}/IGZO$	Thin film	Spin coated	2	8.357×10^2	5.4×10^{12} , 520	128/647 ms	2022 ⁸⁷
$(iBA)_2(MA)_3Pb_4I_{13}$	Thin film	Hot-casted	1.5	1.171×10^{-1}	—, 532	16/15 ms	2018 ⁸¹
DJ phase perovskites							
$(2mepH_2)(MA)Pb_2I_7$	Single crystal	STL	10	13	—, 405	40/— μs	2020 ⁹⁸
$(HDA)CsPb_2Br_7$	Single crystal	STL	10	8.2×10^{-5}	8.1×10^8 , 405	200/300 μs	2020 ⁹⁹
$(4AMP)(MA)_2Pb_3Br_{10}/MAPbBr_3$	Single crystal	STL	0	1.19×10^{-3}	1.26×10^{12} , 405	600/600 μs	2020 ⁸⁴
$(EDA)(MA)Pb_2I_7$	Thin film	Spin coated	2	1.25×10^{-1}	7.1×10^{10} , 532	410/380 μs	2020 ¹⁰⁰
ACI phase perovskites							
$(GA)(FA)PbI_4$	Single crystal	STL	5	10^{-1}	2×10^{10} , 515	49/70 ms	2020 ¹⁰¹
$(R-\beta\text{-MPA})EAPbBr_4$	Single crystal	STL	0	—	1.1×10^{11} , 405	300/330 μs	2022 ⁵¹
$(R\text{-PPA})EACl_4$	Single crystal	STL	5	—	4.5×10^7 , 266	—	2022 ⁵²

V_D , drain voltage; R , responsivity; D^* , specific detectivity; t_r/t_d , temporal response rise time/decay time; LDR, linear dynamic range.

and as a polycrystalline grain boundary, with both hindering charge carrier mobility. Therefore, Dong *et al.* substituted the BA^+ spacer with the branch iBA^+ spacer for the fabrication of layered perovskites using a hot-casting method.⁸¹ The responsivity of the $(iBA)_2(MA)_3Pb_4I_{13}$ photodetector significantly improved to 117.09 mA W^{-1} under a small bias voltage of 1.5 V. Moreover, rising and decay response speeds were significantly faster (about 16 and 15 ms, respectively). These improvements were attributed to the use of a shorter chain length branched spacer, a high-quality film with a larger grain size, and a reduced exciton binding energy in high n -value perovskites. However, stacked nano-sheets can result in interfacial charge carrier scattering and too much quantum confinement is undesirable. In fact, Yu *et al.* fabricated $OA_2FA_{n-1}Pb_nBr_{3n+1}$ (OA = octadecylamine) microplates with FA-acetate/acetic acid solution treatment to limit quantum confinement (Fig. 6b),⁸² thereby (i) increasing 2D perovskite grain size *via* the partial exchange of OA^+ and FA^+ (ii) fusing 2D perovskite microplates forming integrated channels promoting charge carrier transport. Hence, the best demonstrated photodetector produced a very high responsivity of 32 A W^{-1} and reasonable response rise and decay times of 0.25 and 1.45 ms, respectively. In 2019, Xu and colleagues reported the first RP phase $(PA)_2(GA)Pb_2I_7$ perovskite single crystal⁸³ in which the GA^+ cations were confined in the cavity instead of the interlayer spacer (Fig. 6c). This provided a robust in-plane photoresponse, while the insulating PA^+ bilayer spacer performed as a hopping barrier to

effectively suppress the undesirable dark current ($\approx 2.4 \times 10^{-11} \text{ A}$). Therefore, the demonstrated single crystal photodetector produced a high responsivity and detectivity at 47 A W^{-1} and 6.3×10^{12} Jones, respectively.

In 2020, Zhang *et al.* demonstrated a 2D/3D heterostructured self-powered perovskite photodetector.⁸⁴ As shown in Fig. 6d, the heterostructured perovskite single crystal $(4AMP)(MA)_2Pb_3Br_{10}/MAPbBr_3$ was fabricated by tuning the molar compositions of 4-(aminomethyl)piperidinium bromide ($4AMPBr_2$), $MABr$, and $PbBr_2$. The device produced a high detectivity of 1.26×10^{12} Jones at zero bias which is compatible with those of $BiFeO_3$, MoS_2 , and some of the state-of-the-art inorganic photodetectors.^{85,86} Recently, Chen and colleagues integrated $BA_2MA_3Pb_4I_{13}$ with an IGZO thin film transistor (TFT) array demonstrating a phototransistor (Fig. 6e)⁸⁷ with a responsivity and detectivity of 835.7 A W^{-1} and 5.4×10^{12} Jones, respectively, under green light illumination. The $BA_2MA_3Pb_4I_{13}/IGZO$ phototransistor array device was also capable of 64 pixels image detection recognizing the letters “S” and “Z”. Even though the layered perovskite photodetectors (Table 2) have produced comparable responsivity and detectivity to those ($\sim 0.8 \text{ A W}^{-1}$ and $\sim 10^{10}$ Jones) of state-of-the-art Si-based complementary metal-oxide-semiconductor (CMOS) devices,⁸⁸ they are still far from commercialization due to the insufficient integrated pixel number relative to commercial CMOS (6 megapixels with a device size of $\sim 40 \text{ mm}^2$). The mass production of layered perovskite photodetectors may become a

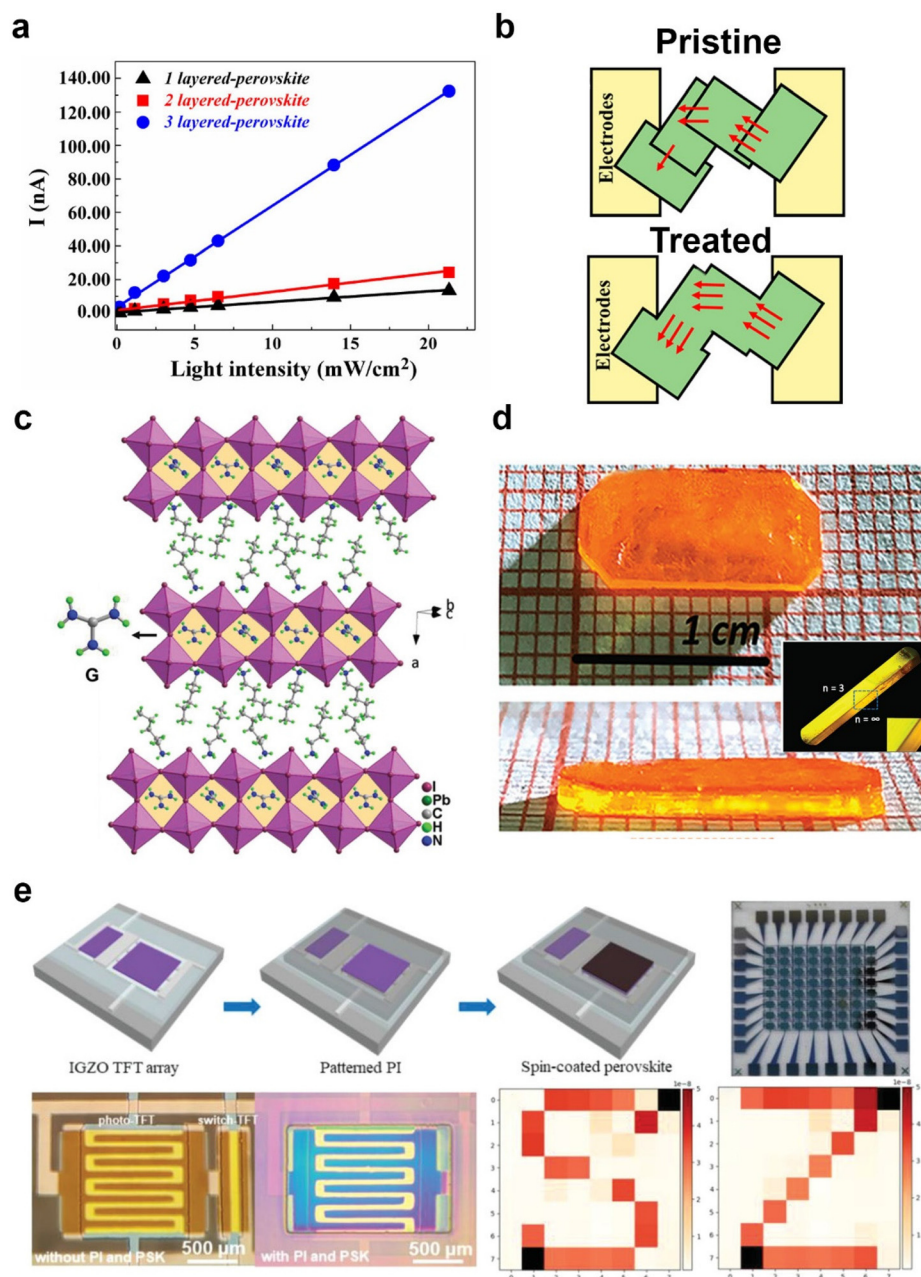


Fig. 6 Application of layered perovskites for photodetectors. (a) Photocurrent as a function of light intensity based on n values (1–3) for the $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ photodetector with a $V_b = 30$ V.⁸⁰ (b) Illustration of the pristine and treated $(\text{OA})_2(\text{FA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ microplate photodetector.⁸² (c) The crystal structure of $(\text{PA})_2(\text{GA})\text{Pb}_2\text{I}_7$.⁸³ (d) Picture of $(4\text{AMP})(\text{MA})_2\text{Pb}_3\text{Br}_{10}/\text{MAPbBr}_3$ heterostructure perovskite single crystal from the top and side views. Inset: optical microscopy image of the crystal boundary when $n = 3$ and $n = \infty$ and the (e) illustration and photos/optical microscope image of $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}/\text{IGZO}$ TFT array at key fabrication steps. Mapping of the letter “S” and “Z” by the integrated 8×8 phototransistor array under illumination.⁸⁷

challenge if they rely on custom-grown single crystals. Therefore, developing a scalable process for fabricating a high pixel integrated layered perovskite phototransistor will be relevant to potential commercialization.

3.3 Field effect transistor

A field-effect transistor (FET) is a widely used electronic device that controls current flow from the drain electrode to the

source electrode under the influence of an applied electric field. The figures of merit, charge carrier (electron or hole) mobility and on/off ratio are vital parameters for evaluating the performance of a FET. The on/off ratio refers to the ratio between the “on” current and the “off”/“dark” current. The “on” state occurs when the gate voltage is larger than the threshold voltage (sufficient for conductivity in the channel between the source and the drain).¹⁰² A high on/off ratio is

desired indicating effective drain and a low on/off ratio can be a sign of the presence of undesirable trap states due to low film quality. The current state-of-art inorganic transistors require deposition processes such as e-beam deposition and atomic layer deposition. Metal halide perovskite FETs may present cost advantages when fabricated by solution processes. Their ambipolar transport properties and high carrier mobilities are also desirable for FETs. In general, FET has four different configurations: top gate top contact (TGTC), top gate bottom contact (TGBC): bottom gate top contact (BGTC), and bottom gate bottom contact (BGBC) (Fig. 7). Typically, a bias voltage is applied to the gate and drain electrodes with the source electrode grounded during operation. In recent years, most of the perovskite thin film FETs have been fabricated in

the BGTC configuration due to their compatibility with the spin coating process while metal electrodes (source and drain) can be evaporated with no more subsequent solution processes. Due to the planar structure of the device, RP phase perovskites, such as PEA_2SnI_4 , (Table 3) with better quantum confinement are more popular compared to the DJ and ACI phases for FET demonstrations due to better horizontal conductivity.

In 1999, the first layered perovskite PEA_2SnI_4 BGBC FET was reported by Kagan *et al.*¹⁰³ producing a saturation hole mobility of $0.62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on/off ratio of 10^4 at room temperature indicating great potential of layered perovskite FETs. In 2002, Mitzi *et al.* demonstrated a melt-processed PEA_2SnI_4 BGBC FET.¹⁰⁴ The device was fabricated by placing

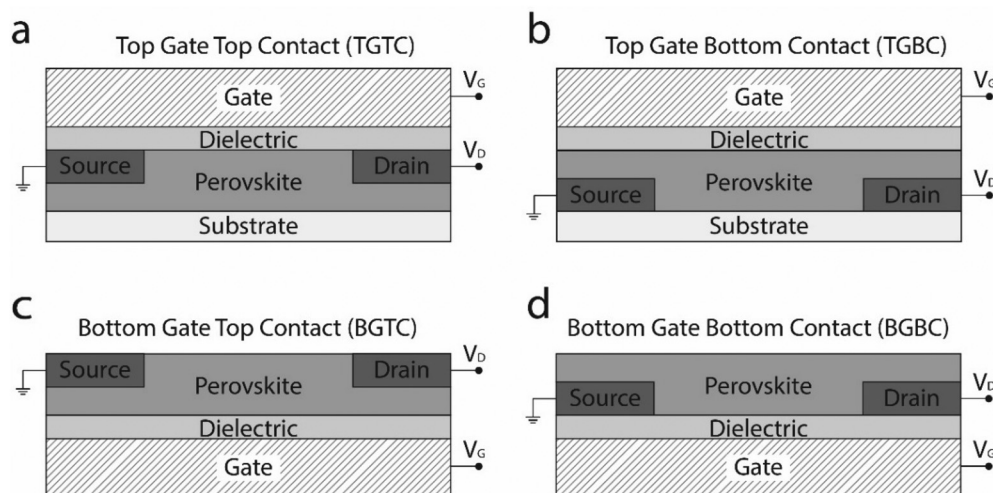


Fig. 7 Schematic of four different field-effect transistor device configurations. (a) Top gate top contact (TGTC), (b) top gate bottom contact (TGBC), (c) bottom gate top contact (BGTC), and (d) bottom gate bottom contact (BGBC).

Table 3 Performance of layered perovskite field-effect transistors at room temperature

Materials	Configuration	Dielectric layer	Drain and source	Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)		On/off ratio	Year ^[ref.]
				Electrons	Holes		
PEA_2SnI_4	BGBC	SiO_2	Pd	—	0.62	10^4	1999 ¹⁰³
$(4\text{-FPEA})_2\text{SnI}_4$	BGBC	SiO_2	Cr/Pd	—	0.2–0.6	$\approx 10^5$	2001 ¹⁰⁹
PEA_2SnI_4	BGBC	SiO_2	Pd	—	0.5	10^5	2001 ¹¹⁰
PEA_2SnI_4	BGBC	SiO_2	Au	—	2.6	10^6	2002 ¹⁰⁴
PEA_2SnI_4	BGTC	SiO_2	Au	—	0.78	4.2×10^5	2004 ¹¹¹
PEA_2SnI_4	TGTC	Cytop	C_{60}/Al	1.5 ± 0.3	—	$(2.4 \pm 6.4) \times 10^4$	2016 ¹¹²
PEA_2SnI_4	TGTC	Cytop	MoO_x/Au	—	12 ± 1	$(1.9 \pm 2.1) \times 10^6$	2016 ³⁰
PEA_2SnI_4	BGTC	SiO_2	Au	—	0.76–1.2	$> 10^3$	2017 ¹¹³
$\text{BA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$	BGTC	SiO_2	Ag	1.25^a	—	$\approx 10^6$	2018 ¹⁰⁵
$(4\text{Tm})_2\text{SnI}_4$	BGTC	SiO_2	Au	—	1.78	$10^5\text{--}10^6$	2019 ¹¹⁴
PEA_2SnI_4	BGTC	PVA/CL-PVP	Au	—	0.30 ± 0.07	$\approx 10^3$	2019 ¹¹⁵
PEA_2SnI_4	BGTC	SiO_2	Au	—	3.51 ± 0.60	3.4×10^6	2020 ¹⁰⁶
$\text{BA}_2\text{MAPb}_2\text{I}_7$	BGTC	SiO_2	Au	0.129 ± 0.048^a	—	$10^6\text{--}10^7$	2021 ¹¹⁶
PEA_2SnI_4	BGTC	SiO_2	Au	—	2.03 ± 0.14	3.4×10^6	2021 ¹¹⁷
TEA_2SnI_4	BGTC	SiO_2	Au	—	0.15	10^4	2022 ¹¹⁸
PEA_2SnI_4	BGTC	SiO_2	Au	—	2.24	$\approx 10^6$	2022 ¹¹⁹
$\text{PEA}_2\text{SnI}_4 + 5 \text{ mol\% SnF}_2$	BGBC	SiO_2	Au/Cr	—	0.68 ± 0.16	10^5	2022 ¹⁰⁷

^a Measured at 77 K for $\text{BA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and 150 K for $\text{BA}_2\text{MAPb}_2\text{I}_7$.

the PEA_2SnI_4 film between a polyimide-treated silicon wafer and a Kapton cover sheet (Fig. 8a) which was heated at 213 ± 5 °C (the melting point of PEA_2SnI_4), and then was further hand-pressed by another heated plate at a temperature 5–10 °C and above. After the melt-process treatment, the film morphology significantly improved with the enlarged grain size producing an enhanced hole mobility of about $2.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ measured at room temperature. In 2018, Li and colleagues reported an n-type perovskite FET using $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1-3$) single crystal flakes.¹⁰⁵ Device fabrication was done by exfoliating as-grown single crystals into flakes with a thickness of 80–100 nm with Scotch tape, which were then transferred onto a 285 nm- SiO_2 -covered-Si substrate. The device produced a maximum electron mobility of 2×10^{-3} , 8.3×10^{-2} , and $1.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $n = 1, 2,$ and 3 , respectively, at 77 K. Although the PL spectra blue shifts were observed to be indicative of phase transition (not shown here), no sudden increase or drop in mobility (Fig. 8b) was observed due to the transition that would otherwise occur in 3D perovskites.

In 2020, Zhu *et al.* demonstrated a self-passivation method by using additional PEAI in PEA_2SnI_4 polycrystalline film.¹⁰⁶ Moreover, metallic Sn additive was added to the PEA_2SnI_4 pre-

cursor to limit undesirable Sn oxidation. The combined benefits allowed the best FET to produce a hole mobility and on/off ratio of $3.51 \pm 0.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 3.4×10^6 , respectively. In addition, the first perovskite-based complementary inverter was also demonstrated by combining an n-channel indium gallium zinc oxide (IGZO) FET with PEA_2SnI_4 BGTC FET (Fig. 8c). The inverter produced a high voltage gain of over 30 with low signal noise. Most recently, Liu *et al.* demonstrated a p-doped PEA_2SnI_4 BGBC FET device by adding SnF_4 , improving hole mobility¹⁰⁷ from 0.25 ± 0.08 to $0.68 \pm 0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after adding 5 mol% SnF_2 additive. No further improvement but performance deterioration was observed when the SnF_2 concentration was further increased to 10 mol% (Fig. 8d).

While layered perovskite FETs have made outstanding progress in recent years (Table 3), there remain challenges and opportunities for further research and development. Firstly, there needs to be a rational design (*e.g.*, development of a model) for choosing the material for different layered perovskites for high-performance FETs. It will be most useful if material choice or the newly developed fabrication strategies can overcome the limited FET mobility demonstrated by the current layered perovskite which currently is well below those

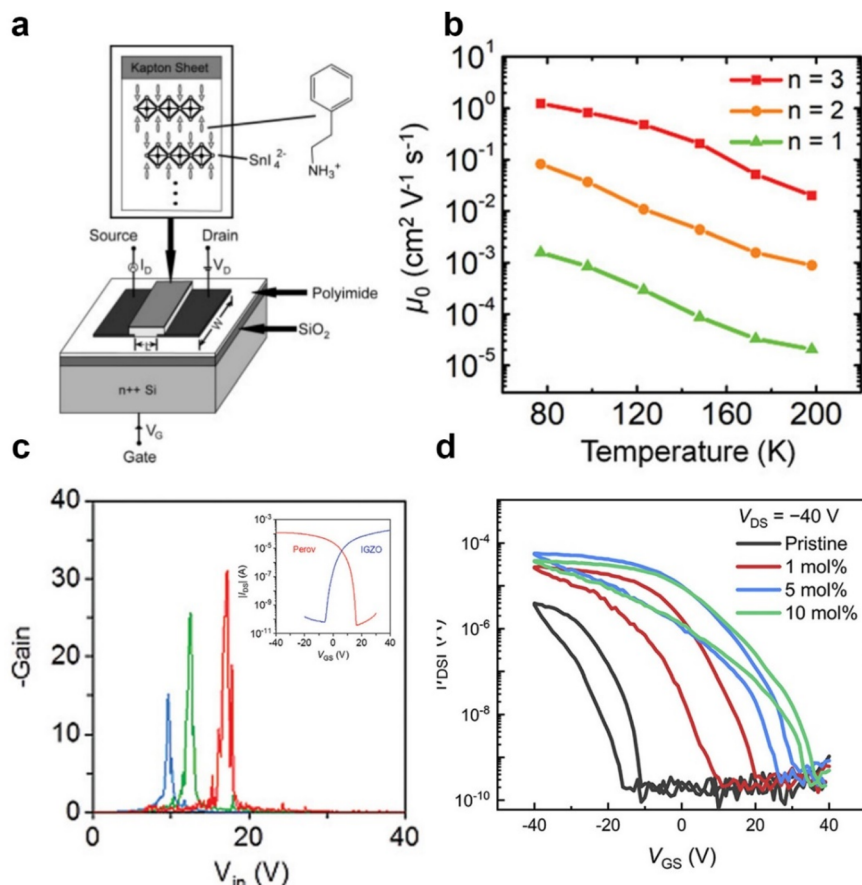


Fig. 8 Application of layered perovskites in field-effect transistors. (a) Illustration of melt-processed PEA_2SnI_4 FET on a silicon substrate. The inset illustrates the cross-section of the PEA_2SnI_4 and Kapton cover sheet.¹⁰³ (b) Measured mobility versus temperature of $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ FET with different n (1, 2, and 3).¹⁰⁵ (c) Gain of the complementary $\text{PEA}_2\text{SnI}_4/\text{IGZO}$ inverter at different direct voltage flows: at 20 (blue), 30 (green), and 40 (red) V. Inset: Transfer characteristics of a $\text{PEA}_2\text{SnI}_4/\text{IGZO}$ inverter.¹⁰⁶ (d) Transfer characteristics of PEA_2SnI_4 with 0–10 mol% SnF_2 additives.¹⁰⁷

of the state-of-arts, e.g., $139.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the best hydrogenated polycrystalline In_2O_3 ($\text{In}_2\text{O}_3\text{:H}$) FET.¹⁰⁸ While a layered perovskite FET is far from commercialization at this stage as device reliability and other manufacturing considerations such as scale up have not been seriously considered, there exist opportunities for further research such as the demonstration of perovskite FET array devices and integration of a perovskite FET with liquid crystal display (LCD), the most relevant application for thin film transistors.

4. Future outlook and conclusion

2D metal halide perovskites have immense potential for optoelectronic applications due to their enabling properties including enhanced stability and diverse choices in functional spacers and crystal phases such as the RP, DJ, and ACI phases. In this review, we have reviewed the rapid progress made for the applications of these phases in solar cells, photodetectors and field effect transistors (FET), and there remain opportunities and challenges requiring further research and development (R&D).

In terms of solar cells using layered perovskites as absorbers, R&D opportunities include: (i) interface and interlayer optimization by a surface passivation layer and development of a self-assembled monolayer for a charge selective layer; (ii) the use of layered perovskites for high and low bandgap solar cells for multi-junction tandem solar cells; and (iii) the development of scalable processes for layered perovskites for large areas or module demonstrations. In addition, we need a better understanding of the real material composition, stoichiometry, presence of gradient rather than pure phases, and grain orientations. Current reports so far rely on nominal concentrations of precursor components for material identification which is limiting. A deeper understanding of the material structure of layered perovskites will enable better engineering to enhance the functionality of spacer cations^{120,121} to improve the performance of not just solar cells but also photodetectors and FETs.

For photodetectors, a new pixel-integrated method compatible with layered perovskites needs to be developed as the current industry method *via* molecular beam epitaxy for the traditional Ge photodetector on a silicon circuit is not compatible with metal halide perovskites. Further work can also be done on achieving better band alignment between the layered perovskite and metal electrode for better charge extraction. In terms of challenges, instability (from halogen ion reactions with metal electrodes forming metal halides (AgI_2 , CuI_2 , or AuI_2)) under a bias voltage (typically 1–10 V) needs to be overcome. This not only impacts photodetectors but also FETs, perhaps more severely due to the higher operational bias (e.g., 10–60 V for typical drain voltage).

For FETs, it will be beneficial for developing a rational material design (e.g., development of models predicting electronic properties that are also relevant to specific FET device operation mechanisms) to expand layered perovskite choices

other than the popular PEA_2SnI_4 at present. There is also an urgent need to improve layered perovskite FET mobility to reach parity with the state-of-the-art thin film transistor (TFT) devices.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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