Lead-free perovskites: growth, properties, and applications

Fan Yang^{1,2}, Aocheng Wang^{1,2}, Shuai Yue^{2,3}, Wenna Du^{2,3}, Shaoli Wang^{2,4*}, Xiaotao Zhang^{1*} and Xinfeng Liu^{2,3*}

ABSTRACT Lead halide perovskites have attracted extensive attention in recent years because of their excellent photoelectronic properties, such as high absorption coefficients, carrier mobilities, defect tolerances, and photoluminescence efficiencies. However, a key issue hindering their commercial application is the toxicity of lead. Replacing lead with other nontoxic elements is a promising solution to this problem. Considering their atomic radii, relative atomic masses, and electron arrangements, perovskites based on Sn, Bi, Sb, and other elements instead of Pb have been widely synthesized. Here, we summarized the growth methods, photoelectric properties, and device applications of these lead-free perovskites. First, we introduced several common growth methods for lead-free perovskites, including solution methods, solid-state reaction, and chemical vapor deposition methods. Second, we discussed the photoelectric properties and methods for optimizing these properties of lead-free perovskites with different structure dimensions. Finally, the applications of lead-free perovskites in solar cells, light-emitting diodes, and X-ray detectors were examined. This review also provides suggestions for future research on lead-free perovskites.

Keywords: lead-free perovskites, growth methods, bandgap, photoluminescence, solar cells

INTRODUCTION

Lead halide perovskites possess a general crystal structure of APbX_3 , where $\text{A} = \text{CH}_3\text{NH}_3^+$ (MA), $\text{CH}(\text{NH}_2)_2^+$ (FA), or Cs^+ , and $\text{X} = \text{Cl}$, Br, or I. These materials have been

extensively researched since the mid-20th century [1–3]. They are widely used in solar cells, light-emitting diodes (LEDs), and piezoelectric or thermoelectric components owing to their strong light absorption capacities, low exciton binding energies and long carrier diffusion lengths [4–8]. In only nine years, the power conversion efficiency (PCE) of photovoltaic devices employing lead halide perovskites has rapidly increased from 3.8% to 25.2% [9–16]. Lead halide perovskite nanomaterials exhibit several advantageous properties, such as high photoluminescence quantum yields (PLQYs), good optical stabilities, narrow emission widths (full width at half maximum, FWHM), and high color purities.

However, lead is a heavy metal that is harmful to the human body, and its toxicity hinders further application. Studies have shown that lead halide perovskite materials produce hydrohalic acids during the oxidation process, further increasing their toxicity to organisms [17]. To avoid toxicity concerns, researchers have attempted to replace lead with various other nontoxic elements.

To date, many significant advances have been achieved in using nontoxic elements to replace lead for lead-free perovskites [18–23]. In this paper, the growth methods, photoelectric properties, and applications of Sn-, Bi-, and Sb-based perovskites are discussed. First, several common methods to synthesize lead-free perovskites are summarized. Then, the photoelectric properties of lead-free perovskites based on different structure dimensions are discussed. Finally, applications of these materials in solar cells, LEDs, and X-ray detectors are considered. This review provides suggestions for the future development of

¹ Tianjin Key Laboratory of Molecular Optoelectronic Science, Department of Chemistry, School of Science, Tianjin 300072, China

² CAS Key Laboratory of Standardization and Measurement for Nanotechnology, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China

³ University of Chinese Academy of Sciences, Beijing 100049, China

⁴ Experiment Center of Forestry in North China, Chinese Academy of Forestry, Beijing 102300, China

* Corresponding authors (emails: liuxf@nanoctr.cn (Liu X); zhangxt@tju.edu.cn (Zhang X); wshaoli@iccas.ac.cn (Wang S))

novel lead-free perovskites.

GROWTH METHODS OF LEAD-FREE PEROVSKITES

Solution methods

Solution-based methods are the most commonly used techniques to synthesize perovskites of various morphologies; they are also easily controlled and inexpensive [24]. In this section, four different methods are introduced: reduced solution saturation, spin-coating, hot injection, and the hydrothermal methods.

Reduced solution saturation method

Many techniques have been applied to reduce the solution saturation point, such as changing the temperature or using an anti-solvent to precipitate crystals. Ju *et al.* [25] reduced the solubility of $\text{MA}_3\text{Sb}_2\text{I}_9$ in a HI acid solution by slowly lowering the temperature. They dissolved CH_3N , HCl , SbCl_3 , and SnO in HI, and heated the mixture at 220°C for 24 h, followed by slow cooling at a rate of 5°C h^{-1} to obtain a Sn-doped $\text{MA}_3\text{Bi}_2\text{I}_9$ single crystal

(SC). Zhang *et al.* [26] placed the $\text{Cs}_3\text{Bi}_2\text{I}_9$ precursor solution on a hot plate covered with aluminum foil containing holes to accelerate the solvent volatilization, as shown in Fig. 1a, and slowly lowered the temperature from 60°C to 50°C over 3 days to obtain a millimeter-scale $\text{Cs}_3\text{Bi}_2\text{I}_9$ SC (Fig. 1b). Owing to the different solubilities of perovskite compounds in various solvents, an anti-solvent crystal growth method was proposed [27,28]. For example, Zuo and Ding [29] reported that NH_4I and SbI_3 were more soluble in ethanol than in CHCl_3 (anti-solvent); therefore, they placed an ethanol solution of $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$ in a beaker of CHCl_3 and sealed it. The evaporation of CHCl_3 accelerated the precipitation of $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$ crystals.

Spin-coating method

The spin-coating process allows the dispersion of a precursor solution on a substrate. As the solvent evaporates, the precursor solution reaches supersaturation and perovskite grains begin to nucleate. In this process, the solvent evaporation rate affects the grain nucleation process. An annealing process is normally adopted to evaporate

Figure 1 (a) Schematic of the reduced solution saturation method used to synthesize $\text{Cs}_3\text{Bi}_2\text{I}_9$ SCs. (b) Digital photograph of $\text{Cs}_3\text{Bi}_2\text{I}_9$ SCs. (a) and (b) are reprinted with permission from Ref. [26]. Copyright 2018, the Royal Society of Chemistry. (c) Synthesis of $\text{Cs}_2\text{AgBiCl}_6$ QDs by the hot injection method. (d) Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of Bi-doped $\text{Cs}_2\text{AgInCl}_6$ NCs and undoped $\text{Cs}_2\text{AgInCl}_6$ NCs. (c) and (d) are reprinted with permission from Ref. [39]. Copyright 2019, the American Chemical Society. (e) Schematic of CsSnX_3 nanowires prepared by CVD. (f) Optical images of CsSnI_3 , CsSnBr_3 , and CsSnCl_3 nanowires. The scale bar is 100 μm . (e) and (f) are reprinted with permission from Ref. [44]. Copyright 2019, the American Chemical Society. (g) Process for the CVD growth of vertically aligned MASnI_3 nanowires on a porous alumina template. Reprinted with permission from Ref. [45]. Copyright 2017, the American Chemical Society.

the solvent more quickly. A uniform and dense film is necessary to achieve excellent device performance. However, it is difficult to obtain a high-quality film using simple spin-coating [30–32].

Hong *et al.* [33] prepared CsSnI_3 thin films using a one-step spin-coating method. They added equal amounts of CsI and SnI_2 to dimethyl sulfoxide (DMSO) to prepare a precursor solution. This precursor solution (50 μL) was spin-coated on indium tin oxide (ITO) glass at a speed of 4000 rpm. After 30 s, toluene was dropped onto the center of the substrate, followed by annealing at 90°C for 10 min to yield a dense black film. In this process, toluene acted as an anti-solvent and was essential in improving the film quality. Xi *et al.* [34] prepared FASnI_3 thin films using a multi-step spin-coating and evaporation process. They used water to dissolve formamidinium iodide (FAI) and then added poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). This FAI/PEDOT:PSS aqueous solution was spin-coated on an ITO substrate coated with PEDOT:PSS, which was then annealed. The addition of PEDOT:PSS produced a less dendritic film structure in which minute spherical FAI crystals were formed. Subsequently, the film was moved to a vacuum chamber for evaporation of SnI_2 and annealed. The FASnI_3 thin film formed was compact with no pinholes observed owing to the large contact area of the small FAI crystal spheres with SnI_2 .

Hot injection method

Hot injection is a universal method to prepare perovskite nanocrystals (NCs) [35–37]. A precursor solution is prepared at high temperatures in nitrogen environment. The precursor solution is then injected into a high-temperature reaction solution at a suitable temperature to rapidly nucleate and grow NCs. After cooling in an ice water bath, the NCs can be recovered by centrifugation. The temperature during injection and the reaction time after injection are key factors governing the morphology of the final products. Jellicoe *et al.* [38] first reported adjustable-bandgap CsSnX_3 NCs synthesized using the hot injection method in 2016. They dissolved SnX_2 powder in trioctyl phosphine, a mildly reductive coordination solvent, to obtain a precursor solution. This solution was injected into a high-temperature Cs_2CO_3 solution containing oleic acid (OA) and oleylamine (OAm) to yield stable CsSnX_3 perovskite NCs. Liu *et al.* [39] synthesized $\text{Cs}_2\text{AgInCl}_6$ quantum dots (QDs) using the hot injection method (Fig. 1c and d). They added BiCl_3 to a precursor solution of $\text{Cs}_2\text{AgInCl}_6$ to realize Bi doping, thus obtaining $\text{Cs}_2\text{AgInCl}_6\text{:Bi}$ QDs exhibiting

broadband orange emission and a high PLQY.

Hydrothermal method

Like the other solution methods, the hydrothermal method is a common technique to prepare perovskite crystals. Typically, it involves placing a precursor solution in a reaction kettle, reacting at a high temperature and pressure, and separating and washing steps to obtain the crystals. Zhou *et al.* [40] synthesized $\text{Cs}_2\text{AgInCl}_6$ SCs using the hydrothermal method. They added HCl to a mixture of CsCl , AgCl , and InCl_3 in a high-pressure reactor. This was heated to 150°C and then cooled to room temperature to induce particle nucleation and growth. White $\text{Cs}_2\text{AgInCl}_6$ crystals were obtained after filtration and washing with ethanol. Zhou *et al.* [41] reported the successful synthesis of low-dimensional perovskite crystals using the hydrothermal method. Equal amounts of SnBr_2 and $\text{C}_4\text{H}_{14}\text{N}_2\text{Br}_2$ powders in a liquid mixture of HBr and H_3PO_2 were heated and stirred. After dissolution and cooling to room temperature, $\text{C}_4\text{N}_2\text{H}_{14}\text{SnBr}_4$ nanowires were obtained.

Solid-state reaction

In general, solid-state reactions include two processes: a reaction at an interface and material migration. This technique is usually employed to mix the reactant particles evenly. At high temperatures, chemical reactions occur on the surface of the reactant to produce a new phase containing structural defects. This is followed by structural adjustment and crystal growth of the new phase. Chung *et al.* [42] obtained CsSnI_3 in a pure orthogonal phase using a solid-state reaction. They mixed CsI and SnI_2 powders in an evacuated Pyrex tube, performed the reaction at 550°C for 1 h, and cooled the tube to room temperature over 6 h to grow SCs. Benin *et al.* [43] placed a solid mixture of CsBr and SnBr_2 particles (molar ratio 4.5:1) in a sealed Pyrex tube and heated it to 350°C for 60 h, after which the tube was opened, and the above process was repeated in a glove box. This procedure produced the pure Cs_4SnBr_6 phase.

Chemical vapor deposition (CVD) method

CVD is used to grow perovskites with various morphologies and few defects. In a simple CVD system, the reactants and substrate are placed in a chamber at a set distance from each other. An inert air flow carries the reactants from the high-temperature region to the low-temperature substrate surface, where deposition occurs. The excess reactants and unreacted precursor gases are discharged from the chamber along with chemical by-

products. Han *et al.* [44] synthesized CsSnX₃ nanowires (Fig. 1f) by CVD. As shown in Fig. 1e, they divided the CVD tube into three regions and placed SnX₂ powder upstream in the airflow, CsX powder midstream, and a mica substrate downstream. The SnX₃, CsX₃, and mica substrate were heated to 220–350, 610–670, and 200–260°C, respectively, in an argon atmosphere, and the pressure in the tube was maintained at 0.16 Torr for 20 min. Waleed *et al.* [45] utilized a porous alumina template as a substrate to grow vertically aligned MASnI₃ nanowires (Fig. 1g). They deposited tin nanoclusters in the nanopores of the template and placed it in a tubular furnace. With Ar as a carrier gas, MAI was deposited in the nanopores to complete the reaction, producing MASnI₃ nanowires. The nanowires were not only regularly shaped, but they also were resistant to water and oxygen owing to their small contact surfaces.

PROPERTIES OF LEAD-FREE PEROVSKITES

Sn(II)-based ABX₃ perovskites

Tin has two predominant valence states, Sn²⁺ and Sn⁴⁺, allowing for the formation of three-dimensional ASn(II)X₃ and zero-dimensional A₂Sn(IV)X₆ perovskite structures. As shown in the crystal structure of ASn(II)X₃ (Fig. 2a), eight coordinated A-site cations are located at the corners, a Sn(II) cation is located at the center, and six nearest-neighbor X anions form eight planes, thus creating an octahedral SnX₆ structure. Each octahedron can be infinitely extended by connecting the vertices to form a three-dimensional perovskite structure. In addition, the tolerance factor (*t*) and the octahedral factor (*μ*) can be calculated using the following formula [38]:

$$t = R_A + \frac{R_B}{\sqrt{2}(R_B + R_X)},$$

$$\mu = \frac{R_B}{R_X},$$

where *R*_A, *R*_B, and *R*_X represent the effective radii of A, B, and X ions. Specifically, tolerance factor *t* should be close to 0.9–1.0 to obtain the cubic-phase crystal structure, and octahedral factor *μ* should exceed 0.41 to maintain stability [46]. Yin *et al.* [47] summarized a series of *t* and *μ* values for common perovskites, as shown in Fig. 2b and c. The *t* value of an organic/inorganic hybrid tin(II) halide perovskite is close to 1; for example, the values for FASnCl₃, MASnCl₃, and CsSnCl₃ are between 0.85 and 0.95. Therefore, the stability of a perovskite can be improved by adjusting the A-site composition without

changing the halogen composition. In addition, if the halogen is changed from Cl to I, the stability decreases. Taking CsSnX₃ as an example, CsSnCl₃ exhibits a highly symmetrical *Pm3m* cubic-phase perovskite structure with superior stability, while CsSnBr₃ and CsSnI₃ exhibit orthorhombic phases that belong to the lower-symmetry *Pnma* space group. This is consistent with the tolerance and octahedral factor calculations. To summarize, the divalent Sn-based halide perovskite crystal structure exhibits a high degree of symmetry.

Like lead halide perovskites, divalent tin perovskites also exhibit adjustable bandgaps. By changing the ratio of the halide composition, the bandgap can be continuously adjusted from 1.69 to 3.34 eV [48]. Yuan *et al.* [49] reported the absorption and photoluminescence (PL) spectra of bulk Sn(II)-based CsSnX₃ perovskite films (Fig. 2d). The emission peak of CsSnCl₃ was close to 440 nm, while that of CsSnBr_{0.5}I_{2.5} was located in the near-infrared region at ~920 nm. When Cs⁺ was substituted with a smaller MA⁺ amino group, the PL peak was slightly blue-shifted. In addition, the ASn(II)X₃ perovskite exhibits excellent photoelectric properties, making it suitable for device fabrication. In 1999, Kagan *et al.* [50] reported the fabrication of high-efficiency field-effect transistors with high carrier mobility, based on layered tin perovskites. Stoumpos *et al.* [51] measured the resistivities of MASnI₃ and FASnI₃ at 300 K to be 0.49 and 11.8 Ω cm, respectively (Fig. 2e and 2f). The electron mobilities of MASnI₃ and FASnI₃ were calculated to be 2320 and 103 cm² V⁻¹ s⁻¹, respectively, according to the formula $\mu = 1 \text{ nep}^{-1}$. As candidate materials for photovoltaic cells, Sn-based perovskites exhibit excellent photoelectric properties, such as high absorption coefficients, long diffusion lengths, and low defect tolerances. Wu *et al.* [52] reported a diffusion length of 1 μm, a bulk carrier lifetime close to 6.6 ns, and a doping concentration of approximately $4.5 \times 10^{17} \text{ cm}^{-3}$ for melt-synthesized CsSnI₃ ingots. Sn(II)-based perovskites are direct-bandgap semiconductors with narrower bandgaps than their lead-based analogs. For example, the bandgap of MASnI₃ ranges from 1.2 to 1.4 eV, suggesting that the absorption spectrum of MASnI₃ can be extended to the near-infrared region [51].

Double perovskites

The molecular formula for double perovskites can be expressed as A₂B'(I)B''(III)X₆, corresponding to a combination of two perovskites of formula AB(II)X₃. These materials are called glaciolite or potassium glaciolite. In double perovskite Cs₂AgInCl₆, the alternating arrange-

Figure 2 (a) Unit cell of the $ASn(II)X_3$ perovskite. Cs^+ and MA^+ represent inorganic and organic cations at the A site. (b) Tolerance factors (t) of various perovskites. (c) Octahedral factors (μ) of various perovskites. (b) and (c) are reprinted with permission from Ref. [47]. Copyright 2019, Wiley. (d) Normalized absorption and steady-state PL spectra of pure- and mixed-halogen $CsSnX_3$ films. Reprinted with permission from Ref. [49]. Copyright 2018, Wiley. Single-crystal resistivities of (e) $MASnI_3$ and (f) $FASnI_3$ in the range of 5–330 K. Reprinted with permission from Ref. [51]. Copyright 2013, the American Chemical Society.

ment of $[AgCl_6]$ and $[InCl_6]$ octahedra forms a double perovskite skeleton, with Cs^+ supported between the octahedra (Fig. 3). Li^+ , Na^+ , K^+ , Rb^+ , Ag^+ , etc., can be employed as the B'(I) ion in double perovskites; Al^{3+} , Ga^{3+} , In^{3+} , Bi^{3+} , Sb^{3+} and some lanthanides can be used as the B''(III) element. However, not every combination forms a corresponding double perovskite. Moreover, because the photoelectric properties of perovskites are primarily determined by the $[BX_6]$ unit, double perovskites composed of two different B elements are significantly more complicated than ABX_3 perovskites.

Cs_2AgBiX_6

In contrast to direct-bandgap inorganic lead halide perovskites, Cs_2AgBiX_6 generally exhibits an indirect bandgap. This is because the valence band maximum (VBM) is moved from the (111) Brillouin zone boundary (the R-point in a primitive cubic cell and the L-point in a face-centered cubic cell) to the X-point. The valence band of

Figure 3 Crystal structures for $CsPbCl_3$ and $Cs_2AgInCl_6$ showing the $[BX_6]$ octahedra present in these $AB(II)X_3$ perovskite-type compounds. The general design principle for chemical unit co-substitution is also shown. Reprinted with permission from Ref. [40]. Copyright 2019, Wiley.

Cs_2AgBiX_6 consists of 3p/4p halogen orbitals and Ag 4d orbitals. The valence-to-conduction-band transition oc-

curs from the 3p/4p halogen state to the anti-bonding Ag 5s and Bi 6p states (Fig. 4a and b) [53]. $\text{Cs}_2\text{AgBiBr}_6$ SC exhibits an indirect bandgap of 1.95 eV, a long room-temperature PL lifetime of 660 ns, and an inherently high defect tolerance (Fig. 4c) [54]. It also displays an obvious thermochromic phenomenon: with increasing temperature, the color of the SC changes from red to black. Experimental results and theoretical calculations showed that the Ag–Br and Bi–Br bond lengths increased during heating, and harmonic fluctuations were observed at high temperatures (Fig. 4d and e). These phenomena, along with the inherently strong electron–phonon and spin–orbit coupling, produced thermochromism. In addition, lattice expansion did not change the phase; the color returned to red when the sample was cooled to room temperature (Fig. 4d) [55]. Li *et al.* [56] reported that

under a pressure of 3 GPa, cubic-phase $\text{Cs}_2\text{AgBiBr}_6$ exhibited $[\text{AgBr}_6]$ and $[\text{BiBr}_6]$ octahedral compression, resulting in orbital overlap and causing bandgap reduction. When the pressure was above 3 GPa, the cubic phase was transformed into a tetragonal phase. The decreased Ag–Br–Bi bond angle reduced the Bi 6p/Ag 4d and Br 4p orbital coupling, increasing the bandgap. When the pressure was released, the bandgap was 8.2% smaller than that observed initially, demonstrating the excellent reversibility of the system (Fig. 4g).

Bekenstein *et al.* [57] observed sharp absorption peaks for $\text{Cs}_2\text{AgBiBr}_6$ at 430 nm and for $\text{Cs}_2\text{AgBiCl}_6$ at 365 nm, 1 eV higher than the band edge energy. They suggested that this difference was due to a localized Bi 6s–6p transition rather than to a confined exciton (Fig. 5a). Yang *et al.* [58] synthesized $\text{Cs}_2\text{AgBiX}_6$ NCs with a tun-

Figure 4 (a) Band structure diagram for $\text{Cs}_2\text{AgBiBr}_6$. (b) Atomic partial density of states plots for $\text{Cs}_2\text{AgBiBr}_6$. (a) and (b) are reprinted with permission from Ref. [53]. Copyright 2016, the American Chemical Society. (c) Time-resolved PL and fits of the PL decay time (τ) for both powder and single-crystal $\text{Cs}_2\text{AgBiBr}_6$ at room temperature. Reprinted with permission from Ref. [54]. Copyright 2016, the American Chemical Society. (d) Images of single-crystal $\text{Cs}_2\text{AgBiBr}_6$ during heating and cooling. (e) Ag–Br and Bi–Br bond lengths varying with temperature. (f) Temperature-dependent cell parameters of SCs: a -axis and cell volume V . (d–f) are reprinted with permission from Ref. [55]. Copyright 2019, Wiley. (g) Left: bandgap variation with pressure for cubic and tetragonal $\text{Cs}_2\text{AgBiBr}_6$. Middle: variation with pressure of the Ag–Br and Bi–Br bond lengths in $\text{Cs}_2\text{AgBiBr}_6$. Right: ratio of the bond angle to the bond length under compression. Reprinted with permission from Ref. [56]. Copyright 2017, Wiley.

able emission range from 395 to 575 nm. The NCs exhibited a sub-bandgap trapping state derived from surface defects, which could be passivated by OA. In addition, a hot-carrier cooling process was observed in $\text{Cs}_2\text{AgBiBr}_6$, competing with sub-bandgap recombination (Fig. 5b–d).

The Na^+ -doped $\text{Cs}_2(\text{Na}_x\text{Ag}_{1-x})\text{BiCl}_6$ double perovskite broke the parity transition rule in $\text{Cs}_2\text{AgBiCl}_6$, transforming from a dark state to a radiative transition and exhibiting over 30-fold enhancement in PL intensity. Na did not contribute to the conduction or valence bands; thus, with increasing Na content, the contribution of Ag to the valence band decreased, increasing the bandgap (Fig. 6) [59]. Yb-doped $\text{Cs}_2\text{AgBiX}_6$ presented good lattice matching with near-infrared emission observed at approximately 1000 nm. This originated from the $\text{Yb}^{3+} {}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ f–f transition, as well as intrinsic trap-state PL. The emission spectra and photon relaxation dynamics of double perovskite NCs can be easily adjusted by controlling the Yb doping concentration [60].

$\text{Cs}_2\text{InAgX}_6$

In $\text{Cs}_2\text{InAgCl}_6$, the bottom of the conduction band is composed of Cl 3p, In 5s, and Ag 5s states, whereas the

top of the valence band is composed of Cl 3p, In 4d, and Ag 4d states. No In s orbital is present at the top of the valence band, creating a direct bandgap. The compound exhibits a direct bandgap of 3.3 eV and belongs to the $Fm3m$ space group, similar to $\text{Cs}_2\text{AgBiX}_6$. $\text{Cs}_2\text{AgInCl}_6$ also displayed a sub-bandgap state. Under UV excitation, the photoinduced defect state emitted light at 2.1 eV [61]. VBM and conduction band minimum (CBM) of $\text{Cs}_2\text{AgInCl}_6$ were even in parity; therefore, a forbidden transition occurred between band edge states at the G point (see the dashed blue arrow in Fig. 7a) [40]. This phenomenon generated dark self-trapping excitons, lowering the PLQY. Luo *et al.* [62] reported a strong Jahn–Teller distortion in the $[\text{AgCl}_6]$ octahedra. They introduced Na ions that did not affect the conduction or valence band, retaining the lattice structure of $\text{Cs}_2\text{AgInCl}_6$.

When an appropriate amount of Na was introduced, the electron wave function symmetry was destroyed, and the electron and hole wave functions overlapped. This disrupted the forbidden transition, and broad white emission with a high PLQY (86%) was observed. However, as the amount of Na was increased further, the

Figure 5 (a) Absorption spectra for $\text{Cs}_2\text{AgBiBr}_6$ and $\text{Cs}_2\text{AgBiCl}_6$ NCs. Insets: $\text{Cs}_2\text{AgBiBr}_6$ NCs suspension and the orange/red $\text{Cs}_2\text{AgBiBr}_6$ bulk crystal. The scale bar is 1 mm. Reprinted with permission from Ref. [57]. Copyright 2018, the American Chemical Society. (b) Absorption spectra for ligand-free and OA-capped $\text{Cs}_2\text{AgBiBr}_6$ NCs. (c) PL spectra for ligand-free and 1% OA-capped NCs. Inset: digital photograph of the colloidal ligand-free $\text{Cs}_2\text{AgBiBr}_6$ NCs. (d) Schematic of the carrier dynamics in $\text{Cs}_2\text{AgBiBr}_6$ NCs. (b–d) are reprinted with permission from Ref. [58]. Copyright 2018, Wiley.

Figure 6 (a–f) Calculated electronic band structures and phonon density of states (PDOSs) for $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{BiCl}_6$ at different values of x : (a, b) $x = 0.25$, (c, d) $x = 0.50$, (e, f) $x = 0.75$. Reprinted with permission from Ref. [59]. Copyright 2019, the American Chemical Society.

electron and hole wave functions were separated, reducing the probability of radiative transitions [62]. Locardi *et al.* [63] incorporated Bi into $\text{Cs}_2\text{Ag}_{1-x}\text{Na}_x\text{InCl}_6$ to produce BiCl_6 states below the CBM. In contrast, in a Na-rich environment, localized AgCl_6 energy levels would be above the VBM. Therefore, in the presence of sufficient Na, the PL was enhanced through trapped emission occurring between states in $[\text{BiCl}_6]$ and $[\text{AgCl}_6]$ octahedra. In addition, Ag doping in $\text{Cs}_2\text{NaInCl}_6$ broke the dark-state self-trapped exciton transition, producing bright yellow PL (PLQY of 31%) [64]. $\text{Cs}_2\text{AgInCl}_6$ exhibited a large direct bandgap, while $\text{Cs}_2\text{AgSbCl}_6$ presented an indirect bandgap. Tran *et al.* [65] reported that for $\text{Cs}_2\text{AgSb}_x\text{In}_{1-x}\text{Cl}_6$, the VBM increased owing to contributions from the Sb $5s^2$ state, while the CBM was lowered because of contributions from the In $5s^0$ and Sb $5p$ states (Fig. 7b). This explained the transition from the indirect to direct bandgap at $x = 0.4$. Moreover, the bandgap of $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ ($x = 0, 0.25, 0.5, 0.75$, and 0.9) was also tuned from indirect to direct [66,67]; as

such, $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ exhibited dual emission. Purple emission (highest PLQY of 36.6%) originated from the indirect bandgap band edge and orange emission was produced upon doping with In (Fig. 7c–e) [66]. In^{3+} can be replaced by doping the $\text{Cs}_2\text{AgInCl}_6$ lattice with Yb^{3+} and Er^{3+} . The characteristic f–f transition emissions were observed in the infrared region at 996 and 1537 nm for the Yb^{3+} and Er^{3+} dopants [68].

Bi, Sb(III)-based $\text{A}_3\text{B}_2\text{X}_9$ layered perovskites

The excellent properties of lead-based perovskites stem from the anti-bonding state formed by the coupling of s orbital of Pb and p orbital of halogen which reduces the ionization energy and allows formation of the conduction band. Elements in the IVA group of the periodic table, which possess the same outermost s orbital and similar atomic weights as Pb, include Bi and Sb. However, Bi and Sb usually exhibit trivalent states; therefore, when these elements are employed in perovskites, the structural formula changes from APbX_3 to $\text{A}_3(\text{Bi/Sb})_2\text{X}_9$ to maintain

Figure 7 (a) Electronic band structure of $\text{Cs}_2\text{AgInCl}_6$. Reprinted with permission from Ref. [40]. Copyright 2017, the Royal Society of Chemistry. (b) Schematic of the bonding and anti-bonding bands in $\text{Cs}_2\text{AgSb}_x\text{In}_{1-x}\text{Cl}_6$ (upper part) and the proposed band diagram (lower part). Reprinted with permission from Ref. [65]. Copyright 2017, the Royal Society of Chemistry. (c) PL spectra for $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ ($x = 0$ and 0.9) NCs. Inset: digital image showing the PL emission of $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ NCs ($x = 0$ and 0.9). (d) Digital photographs of the PL emission for $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ NCs ($x = 0, 0.25, 0.5, 0.75$, and 0.9). (e) PL spectra for $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ NCs ($x = 0, 0.25, 0.5, 0.75, 0.9$). (c–e) are reprinted with permission from Ref. [66]. Copyright 2018, the American Chemical Society.

charge balance. This arrangement usually produces two types of structures: a two-dimensional layered structure with $[\text{BX}_6]$ as the primary unit, and a zero-dimensional structure with $[\text{B}_2\text{X}_9]$ as the primary unit. The two-dimensional structure exhibits a direct bandgap, with superior electron and hole mobilities and a higher defect tolerance compared with those of the zero-dimensional structure.

Bi(III)-based $\text{A}_3\text{B}_2\text{X}_9$ layered perovskites

The structure of $\text{A}_3\text{Bi}_2\text{X}_9$ perovskites is related to the A-site cation and the halogen element. The structure of layered $\text{A}_3\text{B}_2\text{X}_9$ can be obtained by removing the $[\text{BX}_6]$ octahedra from every third layer of the three-dimensional

ABX_3 structure along the $\langle 111 \rangle$ direction. $\text{Rb}_3\text{Bi}_2\text{I}_9$ exhibits a two-dimensional layered structure and belongs to the $P2_1/n$ space group. As the atomic radius of Rb is smaller than that of Cs, $\text{Cs}_3\text{Bi}_2\text{I}_9$ presents a zero-dimensional dimer structure, belonging to the $P6_3/mmc$ space group. Its structural unit is composed of a $[\text{Bi}_2\text{I}_9]^{3-}$ anion cluster. The independent $[\text{Bi}_2\text{I}_9]^{3-}$ anion cluster comprises two $[\text{BiI}_6]^-$ octahedra face-to-face (Fig. 8a). Similarly, in $\text{Cs}_3\text{Bi}_2\text{X}_9$, when $\text{X} = \text{I}$ and Br , a zero-dimensional and a two-dimensional structure, respectively, are formed. For the layered compounds, direct bandgaps of 2.17 eV ($\text{K}_3\text{Bi}_2\text{I}_9$) or 2.16 eV ($\text{Rb}_3\text{Bi}_2\text{I}_9$) were obtained from the theoretical Heyd–Scuseria–Ernzerhof (HSE) and spin-orbit coupling (SOC) calculations. The lowest conduc-

Figure 8 (a) Crystal structures of $\text{Cs}_3\text{Bi}_2\text{I}_9$ (left) and $\text{Rb}_3\text{Bi}_2\text{I}_9$ (right). Reprinted with permission from Ref. [69]. Copyright 2015, the American Chemical Society. (b) Absorption spectra for $\text{Cs}_3\text{Bi}_2\text{I}_{9-x}\text{Br}_x$ films. (c) X-ray diffraction (XRD) patterns for $\text{Cs}_3\text{Bi}_2\text{I}_{9-x}\text{Br}_x$ films. (d) Tauc plots for $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{I}_6\text{Br}_3$, and $\text{Cs}_3\text{Bi}_2\text{Br}_9$ films. (b–d) are reprinted with permission from Ref. [70]. Copyright 2019, the Royal Society of Chemistry. (e) Absorption and PL spectra for $\text{Cs}_3\text{Bi}_2\text{Br}_9$ QDs. Insets: digital images of the QD solution in ambient light and under illumination using a 325-nm UV lamp. Reprinted with permission from Ref. [75]. Copyright 2018, Wiley. (f) Model of Cl-passivated $\text{MA}_3\text{Bi}_2\text{Br}_9$ QDs. (g) Digital photographs of $\text{MA}_3\text{Bi}_2\text{Cl}_3\text{Br}_{9-x}$ QD solutions under illumination using a 325-nm UV lamp. (f) and (g) are reprinted with permission from Ref. [79]. Copyright 2018, the American Chemical Society. (h) Tauc plots for $\text{Cs}_3\text{Sb}_2\text{I}_9$ (left) and $\text{Cs}_3\text{Sb}_2\text{Cl}_3\text{I}_6$ (right). Reprinted with permission from Ref. [84]. Copyright 2020, Elsevier. (i) Proposed band structure diagram for $\text{Cs}_3\text{Sb}_2\text{Br}_9$ QDs. Reprinted with permission from Ref. [87]. Copyright 2017, the American Chemical Society.

tion-band dispersion was moderate, while the highest valence band was extremely flat, indicating that the effective mass of electrons was lower than that of holes. Moreover, the high Born effective charges induced by the instability of the Bi^{3+} $6s^2$ lone electron pair suggested potentially higher carrier mobilities [69].

Yu *et al.* [70] synthesized a series of $\text{Cs}_3\text{Bi}_2\text{I}_{9-x}\text{Br}_x$ thin films. As x increased from 0 to 9, the absorption edge shifted from 556 to 580 nm and then returned to 475 nm. The absorption spectrum of $\text{Cs}_3\text{Bi}_2\text{I}_7\text{Br}_2$ displayed two peaks at ~480 and 580 nm, indicating that two-phase separation occurred (Fig. 8b). From theoretical calculations and experimental characterization, when $x = 3$, $\text{Cs}_3\text{Bi}_2\text{I}_{9-x}\text{Br}_x$ was completely transformed from the $P6_3/mmc$ to the $P3m$ phase. $\text{Cs}_3\text{Bi}_2\text{I}_6\text{Br}_3$ exhibited the narrowest bandgap of 2.05 eV, significantly lower than

that of $\text{Cs}_3\text{Bi}_2\text{I}_9$ (2.23 eV; Fig. 8c and d). In addition, the $\text{Cs}_3\text{Bi}_2\text{I}_6\text{Br}_3$ film possessed larger crystal grains and presented a higher crystallinity, beneficial for photovoltaic applications. Iodine incorporation in $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ caused the structure to transform from one-dimensional chains to a two-dimensional vacancy-ordered structure [71]. The two-dimensional structure showed a larger energy band dispersion bonding strength. Iodine doping increased the anti-bonding energy of the Bi s and Cl p orbitals in the valence band and reduced the bandgap. $(\text{NH}_4)_3\text{Bi}_2\text{I}_9$ powder sample presented a direct bandgap of 2.04 eV [72]. Single-crystal $(\text{NH}_4)_3\text{Bi}_2\text{I}_9$ was easily grown in a low-temperature solution, and exhibited an anisotropic response to X-ray irradiation [73].

A self-trapping state was present in $\text{Cs}_3\text{Bi}_2\text{Br}_9$ QDs, which lowered the PLQY. Yang *et al.* [74] added OA

during the preparation process to passivate the surface defects, improving the PLQY to 4.5%. Leng *et al.* [75] (Fig. 8e) used ethanol as an anti-solvent to prepare $\text{Cs}_3\text{Bi}_2\text{Br}_9$ QDs that presented blue emission at 410 nm with a PLQY of 19.4%. Cao *et al.* [76] used γ -butyrolactone (GBL) as a precursor solvent to synthesize $\text{Cs}_3\text{Bi}_2\text{Br}_9$ QDs. GBL possesses a small Gutmann donor number, allowing effective combination of the metal cation and the halogenated ion, thereby controlling the crystallization process precisely. Tetrabutylammonium bromide (TBABr) was also added to a precursor solution. The bromide ions in TBABr were involved in the formation of the $[\text{BiBr}_6]$ octahedra, enabling attachment of alkyl chains to the QD surface. All these strategies improved the PLQY to approximately 40%. $\text{Cs}_3\text{Bi}_2\text{Br}_9$ nanoplatelets of size 60–250 nm were quantum confined, such that their PL peak was blue-shifted. Moreover, a sharp exciton peak was observed, in contrast to $\text{Cs}_3\text{Bi}_2\text{Br}_9$ SCs [77].

$\text{MA}_3\text{Bi}_2\text{Br}_9$ QDs were dominated by exciton recombination with a PLQY of 12% [78]. Because the $\text{MA}_3\text{Bi}_2\text{Br}_9$ and $\text{MA}_3\text{Bi}_2\text{Cl}_9$ structures were incompatible, Leng *et al.* [79] added Cl^- in the synthesis of $\text{MA}_3\text{Bi}_2\text{Br}_9$ QDs. The Cl^- attached to the surface of $\text{MA}_3\text{Bi}_2\text{Br}_9$ QDs, thus passivating them. At a Cl content of 33.3%, the time-resolved PL spectra of the QDs could be fitted using a single exponential function, indicating that perfect surface passivation was achieved, with a PLQY of 54.1% (Fig. 8f and g). $\text{FA}_3\text{Bi}_2\text{Br}_9$ QDs synthesized by a ligand-assisted re-precipitation method presented a relatively large exciton binding energy with a direct bandgap of 2.87 eV. This was due to the strong quantum confinement effect induced by passivating the QDs surface with OAm and OA ligands, suggesting that this material could be used in LEDs [80].

Bi-based perovskites exhibit good stabilities. $\text{Cs}_3\text{Bi}_2\text{Br}_9$ QDs retained 80% of their PL intensity after 78 h of continuous irradiation by ultraviolet (UV) light, demonstrating their excellent light stability. In addition, the BiOBr generated when a proper amount of water was added to an ethanol solution of $\text{Cs}_3\text{Bi}_2\text{Br}_9$ QDs and passivated the surface defects of the QDs, almost doubling their PL intensity [75]. The addition of a small amount of ethanol to the $\text{MA}_3\text{Bi}_2\text{Br}_9$ QD solution had little impact on their PL properties and would thus benefit the fabrication of the top organic electron (hole) transport layer in LEDs [78].

Sb(III)-based $A_3B_2X_9$ layered perovskites

Sb is located in the same main group of the periodic table

as Bi, but it possesses a smaller relative atomic mass. In addition to cation and halide ion selection, numerous synthetic methods allow the transformation of $A_3\text{Sb}_2\text{X}_9$ from a zero-dimensional to a two-dimensional structure. For example, Saparov *et al.* [81] controlled the annealing temperature during the preparation of a $\text{Cs}_3\text{Sb}_2\text{I}_9$ film. Giesbrecht *et al.* [82] employed $\text{Sb}(\text{OAc})_3$ (OAc^- : CH_3COO^-) as an antimony precursor. As every antimony atom coordinated with seven oxygen atoms in $\text{Sb}(\text{OAc})_3$, such that adjacent Sb atoms were 4.9 Å apart and thereby producing a structure larger than that of SbI_3 . Layered $\text{MA}_3\text{Sb}_2\text{I}_9$ was formed after the addition of MAI. Like Bi, replacing the iodide ion in $\text{MA}_3\text{Sb}_2\text{I}_9$ with chloride allowed a dimensional structure change [83,84]. In addition, choosing a cation with a small radius led to dimer phase transformation to a layered phase [85]. The modification of a layered $\text{Cs}_3\text{Sb}_2\text{I}_9$ film produced a direct bandgap of 2.05 eV [81], while dimer-phase $\text{Cs}_3\text{Sb}_2\text{I}_9$ displayed an indirect transition at 1.95 eV as well as a direct transition at 2.37 eV. After chloride substitution, $\text{Cs}_3\text{Sb}_2\text{Cl}_3\text{I}_6$ exhibited a smaller direct bandgap of 2.05 eV, close to the indirect bandgap (Fig. 8h) [84]. $\text{Cs}_3\text{Sb}_2\text{I}_9$ NCs presented a sharp emission peak in the red-yellow region with many-body exciton interactions and a high absorption cross-section of $1.1 \times 10^{-15} \text{ cm}^2$ [86]. Zhang *et al.* [87] reported that $\text{Cs}_3\text{Sb}_2\text{Br}_9$ QDs exhibited a high exciton binding energy of 530 meV, and that excess Br effectively passivated the surface defect states, resulting in a high PLQY of 46% (Fig. 8i). Compared with bulk SCs, the emission peak of $\text{Rb}_3\text{Sb}_2\text{I}_9$ nanoparticles was blue-shifted with a smaller FWHM of 21 nm, which is the narrowest emission peak reported to date for lead-free perovskite materials [88].

Two-dimensional Sn(II)-based perovskites

Three-dimensional tin perovskites like MASnI_3 can be self-doped (p-type) by the easy oxidation of Sn^{2+} to Sn^{4+} , exhibiting metal conductivity [89–91], which is unfavorable for device performance. Mitzi *et al.* [92] reported that the metal conductivity of a three-dimensional organic tin halide perovskite could be suppressed by reducing the crystal structure dimension. Two-dimensional tin perovskites are composed of organic and inorganic components, allowing additional structural variability, greater anisotropy, and unique optical and electrical properties.

Compared with the three-dimensional tin(II) perovskite, the two-dimensional tin(II) perovskite $(\text{PEA})_2\text{SnI}_4$ ($\text{PEA} = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3^+$) exhibited a smaller bandgap of ~1.26 eV due to the quantum con-

finement effect. The confinement of electrons and holes in the two-dimensional structure increased the recombination probability; therefore, $(\text{PEA})_2\text{SnI}_4$ presented a longer PL decay lifetime (Fig. 9a) [93]. Zhang *et al.* [94] reported that the two-dimensional structure formed by $\text{C}_{18}\text{H}_{35}\text{NH}_3^+$ (OAm^+) and $[\text{SnBr}_6]$ octahedra in $(\text{OAm})_2\text{SnBr}_4$ impeded the formation of electron bands between

$[\text{SnBr}_6]$ units, resulting in strong Stokes shift and high PLQY (Fig. 9b and c). Bi^{3+} and Sn^{2+} possess similar ionic radii, and Bi doping did not change the phase in $\text{PEA}_2\text{SnBr}_4$ [95]. Doping with 0%–20% Bi had little effect on the bandgap. Bi-doped $\text{PEA}_2\text{SnBr}_4$ produced non-intrinsic self-trapping excitons as a result of local lattice inhomogeneity. Self-trapping exciton emission peaks

Figure 9 (a) Crystal structure of $(\text{PEA})_2\text{SnI}_4\text{Br}_{4-x}$. Reprinted with permission from Ref. [93]. Copyright 2017, the American Chemical Society. (b) Digital photograph of an $(\text{OAm})_2\text{SnBr}_4$ perovskite colloidal suspension (left) and film (right) under illumination using a UV light. (c) Normalized absorption, PL excitation, and PL spectra for the $(\text{OAm})_2\text{SnBr}_4$ perovskite film. (b) and (c) are reprinted with permission from Ref. [94]. Copyright 2018, the American Chemical Society. (d) Optical diffuse reflectance spectra and (e) room-temperature PL spectra for Bi-doped $\text{PEA}_2\text{SnBr}_4$ containing different Bi concentrations ranging from 0% to 20%. Insets show corresponding digital photographs of the powders. Reprinted with permission from Ref. [95]. Copyright 2019, Elsevier.

were observed in addition to the free exciton emission (Fig. 9d and e). In contrast to organic ammonium ion, the hydrogen bonding between the imidazole derivative and $[\text{SnI}_6]$ octahedra in Bn_2SnI_4 (Bn = benzimidazolium) was symmetric, resulting in a small distortion of the $[\text{SnI}_6]$ octahedra and a smaller direct bandgap of 1.8 eV. The partial substitution of Pb with Sn formed a solid solution and allowed adjustment of the bandgap in the visible wavelength range [96]. The low PLQY of two-dimensional Sn perovskites was attributed to strong exciton-phonon interactions [97]. Different cations can change the material stability by interacting with $[\text{SnX}_6]$ units. When close aligned bulky stilbene derivatives (2-(4-(3-fluoro)stilbenyl) ethan ammonium iodide (FSAI)) were used as organic cations, unique face-to-face interactions were present, such as face-to-face hydrogen bonding, $\text{CH}\cdots\text{X}$ hydrogen bonding, and interlayer $\text{F}\cdots\text{F}$ interac-

tions. These generated superior air and water stability compared with those of three-dimensional Sn-based perovskites [98].

Bi, Sb(III)-based $\text{A}_3\text{B}_2\text{X}_9$ dimer perovskites

Zero-dimensional structures are also suitable for Bi and Sb substitution. For example, $\text{Cs}_3\text{Bi}_2\text{I}_9$ consists of $[\text{Bi}_2\text{I}_9]$ clusters surrounded by Cs cations and belongs to the $P6_3/mmc$ space group, as shown in Fig. 10a [99]. A $\text{MA}_3\text{Bi}_2\text{I}_9$ film exhibited a direct bandgap of 2.9 eV and an exciton binding energy of 400 meV. Phonon density of states (PDOSs) results showed two separate conduction bands with a gap of 0.5 eV. The lower conduction band extended the bismuth and iodide states, while the higher conduction band was primarily composed of Cs–I hybrid states. The effective masses of electrons and holes were obtained based on the band structures of the VBM and

Figure 10 (a) Crystal structure of Bi, Sb(III)-based $\text{A}_3\text{B}_2\text{X}_9$ dimer-phase perovskites. Reprinted with permission from Ref. [99]. Copyright 2015, Wiley. Calculated density of states (DOSs) for (b) $\text{Cs}_3\text{Bi}_2\text{I}_9$ and (c) $\text{MA}_3\text{Bi}_2\text{I}_9$ perovskites. Reprinted with permission from Ref. [100]. Copyright 2016, the American Chemical Society. (d) Tauc plot for $\text{Cs}_3\text{Bi}_2\text{I}_9$. (e) Thermogravimetric analysis plot and first-order derivative for single-crystal $\text{Cs}_3\text{Bi}_2\text{I}_9$. (f) Current-voltage curve for a hole-only $\text{Cs}_3\text{Bi}_2\text{I}_9$ device. (d–f) are reprinted with permission from Ref. [101]. Copyright 2020, Springer Nature. (g) Upper part: photothermal deflection spectroscopy (PDS) measurements for Bi-based perovskites and $\text{MA}_3\text{Sb}_2\text{I}_9$. Lower part: normalized absorbance of $\text{MA}_3\text{Sb}_2\text{I}_9$ (from PDS) with the calculated Urbach tail energy indicated and the corresponding PL spectrum. Reprinted with permission from Ref. [103]. Copyright 2016, the American Chemical Society. (h) Digital photographs of $\text{MA}_3\text{Sb}_2\text{I}_9$ (left) and Sn-doped $\text{MA}_3\text{Sb}_2\text{I}_9$ (right). (i) Total DOS and partial DOS of intrinsic $\text{MA}_3\text{Sb}_2\text{I}_9$ (upper part) and Sn-doped $\text{MA}_3\text{Sb}_2\text{I}_9$ (lower part). (h) and (i) are reprinted with permission from Ref. [25]. Copyright 2019, the Royal Society of Chemistry.

CBM (Fig. 10b and c) [100]. Zhang *et al.* [101] synthesized $\text{Cs}_3\text{Bi}_2\text{I}_9$ SCs with a bandgap of 1.96 eV and superior thermal and moisture stabilities compared with those of Pb-based two-dimensional perovskites. Furthermore, the trap density of $\text{Cs}_3\text{Bi}_2\text{I}_9$ was $1.4 \times 10^{10} \text{ cm}^{-3}$, considerably lower than those of common inorganic semiconductors, such as polysilicon, Cd, and Te (Fig. 10d–f). Pious *et al.* [102] employed benzylammonium as a cation. They observed that benzyl cation polarization reduced the dielectric mismatch between $[\text{Bi}_2\text{I}_9]$ and the organic cations.

Compared with Bi-based perovskites, the absorption spectrum of $\text{MA}_3\text{Sb}_2\text{I}_9$ did not display obvious exciton absorption, indicating a lower exciton energy. $\text{MA}_3\text{Sb}_2\text{I}_9$ exhibited an absorption coefficient above 10^5 cm^{-1} with a bandgap of 2.14 eV. The weak PL was located at ~560 meV, away from the band edge, suggesting radiative recombination involving sub-bandgap states. This was further supported by the relatively high Urbach tail energy (62 meV) (Fig. 10g) [103]. Ju *et al.* [25] successfully doped single-crystal $\text{MA}_3\text{Sb}_2\text{I}_9$ with Sn, where Sb was replaced by Sn in the unit cell. The upper valence band of Sn-doped $\text{MA}_3\text{Sb}_2\text{I}_9$ comprised the Sn 5s and I 5p orbital bonding states, significantly reducing the bandgap. A substantially red-shifted absorption peak at 296 nm was

observed for Sn-doped $\text{MA}_3\text{Sb}_2\text{I}_9$ and the carrier mobility was approximately doubled (Fig. 10h and i). Moreover, adding HI to $\text{MA}_3\text{Sb}_2\text{I}_9$ films allowed valence-band tuning and improved the morphologies of the films [104,105]. Cation choice also influences the properties of $\text{A}_3\text{Sb}_2\text{X}_9$. For example, the ordered-disordered transformation that occurs in *N*-methylpyrrolidinium significantly affected the ferroelectricity of $(N\text{-methylpyrrolidinium})_3\text{Sb}_2\text{Br}_9$ [106].

Sn(IV)-based A_2SnX_6 perovskites

Sn(IV)-based perovskites possess the chemical formula A_2SnX_6 . Their structure can be considered as the vacancy-ordered ABX_3 structure with the adjacent B atoms removed. Zhou *et al.* [107] described the crystal structure of Cs_2SnI_6 (Fig. 11a). The isolated $[\text{BX}_6]$ octahedron was bridged by Cs^+ , generating a quantum-confined structure, enhancing the PL. The stable tin(IV) oxidation state renders high symmetry, air stability, and excellent photoelectric properties of $\text{A}_2\text{Sn(IV)X}_6$ perovskites. Maughan *et al.* [108] compared a series of A_2SnI_6 compounds ($\text{A} = \text{Cs}^+$, MA^+ , or FA^+). These three compounds exhibited the cubic space group structure shown in Fig. 11b. When the larger MA^+ and FA^+ ions were introduced at the A-site,

Figure 11 (a) Crystal structure of $\text{A}_2\text{Sn(IV)X}_6$. Reprinted with permission from Ref. [107]. Copyright 2019, Wiley. (b) XRD patterns for the A_2SnI_6 series ($\text{A} = \text{Cs}^+$, MA^+ , or FA^+). (c) Structures of Cs_2SnI_6 , MA_2SnI_6 , and FA_2SnI_6 . (b) and (c) are reprinted with permission from Ref. [108]. Copyright 2018, the American Chemical Society. (d) Normalized absorbance (black), excitation (red), and emission (blue) spectra for the as-synthesized $\text{Cs}_2\text{SnCl}_6:0.11\% \text{ Bi}$ (left) and $\text{Cs}_2\text{SnCl}_6:2.75\% \text{ Bi}$ (right). (e) Room-temperature PLQYs of the $\text{Cs}_2\text{SnCl}_6:x \text{ Bi}$ samples ($x = 0\%$, 0.11% , 1.16% , 2.75% , 3.39% , 4.18% , and 6.63%). Inset: digital photographs of the $\text{Cs}_2\text{SnCl}_6:x \text{ Bi}$ samples under illumination using a 365 nm UV light. (f) Calculated formation enthalpies (ΔH) of neutral Bi_i , Bi_{Sn} , and $\text{Bi}_{\text{Sn}} + \text{V}_{\text{Cl}}$ as a function of the chemical potentials. (d–f) are reprinted with permission from Ref. [114]. Copyright 2018, Wiley.

the volume of the unit cell and the I–I contact distance between the $[\text{SnI}_6]$ octahedra increased, as shown in the refined structure (Fig. 11c). Funabiki *et al.* [109] reported that the structures of MA_2SnI_6 powder and film were consistent with the above results. Furthermore, the authors determined that the (111) plane was the most energy-stable surface. Maughan *et al.* [110] compared the aforementioned A_2SnI_6 series with Rb_2SnI_6 . Rb_2SnI_6 possessed a tetragonal perovskite structure ($P4/mnc$) at 295 K that was distorted to a low-symmetry monoclinic perovskite structure ($P2_1/n$) at 100 K, while no temperature-dependent octahedral distortion was observed in Cs_2SnI_6 . The tolerance factors (t) of Cs_2SnI_6 , MA_2SnI_6 , FA_2SnI_6 and Rb_2SnI_6 were calculated to be 0.998, 1.07, 1.16, and 0.959, respectively.

Cs_2SnI_6 , MA_2SnI_6 , FA_2SnI_6 , and Rb_2SnI_6 were considered n-type semiconductors. The Rb-substituted Sn(IV) perovskite had significantly lower carrier mobility than Cs_2SnI_6 . In general, the electronic properties of vacancy-ordered double perovskites are determined by their lattice dynamics. Based on a geometric model of the perovskite tolerance factor, the interaction between octahedral tilt and charge transport in the A_2SnI_6 series was summarized. This was used to predict the charge transfer behavior in vacancy-ordered double perovskites. Materials with tolerance factors closer to 1 exhibited higher carrier mobilities. In the light of the abovementioned tolerance factors, Cs_2SnI_6 , MA_2SnI_6 , FA_2SnI_6 , and Rb_2SnI_6 exhibited maximum carrier mobilities of approximately 9, 2, 0.36, and $0.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively [108,111].

The Sn(IV)-based perovskite A_2SnX_6 exhibits better stability than the Sn(II)-based perovskite. However, the reported PLQYs of these compounds are low. The PLQY of Cs_2SnI_6 was 0.48%, considerably lower than those of lead-based perovskites [112]. Doping is an effective method to control the physical properties of metal halide perovskites and to confer new properties to the material [113]. Tan *et al.* [114] doped the vacancy-ordered double perovskite Cs_2SnCl_6 with Bi^{3+} and compared the PL performances of the samples containing different doping ratios. The results showed that the undoped sample presented no PL, while the PL performances of the doped samples were significantly improved. Fig. 11d–g show that the best doping ratio of Bi was 2.75%, with a PL peak at $\sim 455 \text{ nm}$; the material showed a PLQY of 78.9%, close to those of lead-based perovskites [115]. Bi ions were incorporated at the Sn site in a Cs_2SnCl_6 matrix, as confirmed by material characterization and first-principles calculations. A $\text{Bi}_{\text{Sn}} + \text{V}_{\text{Cl}}$ defect complex was formed, resulting in strong blue emission. The basic properties of

lead-free perovskites are summarized in Table 1.

PHOTOELECTRIC DEVICE APPLICATIONS

Solar cells

Sn-based perovskite solar cells

The radii of the IVA ions Sn^{2+} (1.35 Å) and Pb^{2+} (1.49 Å) are similar. Thus, significant lattice distortion does not occur when lead is replaced with tin in perovskite materials [116]. The optical bandgaps of tin-based perovskites are narrower than those of lead-based perovskites, indicating that the absorption wavelength of tin-based perovskites can range from 800 to 950 nm [51]. Extensive research on tin-based perovskite solar cells (PSCs) has been performed. In 2014, Hao *et al.* [117] used MASnI_3 to prepare tin-based PSCs that achieved a PCE of 5.73%. Koh *et al.* [118] employed FASnI_3 with added SnF_2 as a light-absorbing material in solar cells, realizing an efficiency of 2.10%. Many methods to optimize the efficiency of solar cells by improving the perovskite absorber layer have been reported.

Ogomi *et al.* [119] introduced SnI_2 to the MAPbI_3 structure to prepare a $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite. Optoelectronic devices prepared with this material exhibited a spectral response up to 1060 nm (Fig. 12a), a short-circuit current density (J_{sc}) of 20.04 mA cm^{-2} , and a maximum PCE of 4.18%. Hao *et al.* [120] prepared a series of $\text{MASn}_{1-x}\text{Pb}_x\text{I}_3$ perovskites with adjustable bandgaps of 1.17–1.55 eV, achieved by mixing tin and lead (Fig. 12b). Mixed tin–lead materials showed significantly improved carrier transport characteristics compared with MAPbI_3 [121]. Lee *et al.* [122] observed that at a Sn content of 60% in the mixed tin–lead perovskite, carrier recombination was drastically weakened, the photoelectric output stability was enhanced, and the PCE of the device reached 13.4% (Fig. 12c). Wang *et al.* [123] used a two-step solution method to prepare a dense $\text{FA}_{0.7}\text{MA}_{0.3}\text{Sn}_{0.3}\text{Pb}_{0.7}\text{I}_3$ film with a bandgap of 1.26 eV on the hydrophobic hole-transporting material, with a PCE of 13.6%.

Hao *et al.* [124] reported the effect of the solvent in the crystallization process of MASnI_3 films. When DMSO was used, a uniform, non-porous film was prepared, and the device exhibited a J_{sc} value of 21 mA cm^{-2} . Weiss *et al.* [125] employed a two-step method, combined with vapor deposition, to synthesize a MASnI_3 perovskite film that exhibited significantly enhanced chemical stability in air and under light illumination. Research on the interface between MASnI_3 and TiO_2 determined that the surface

Table 1 Basic properties of lead-free perovskites

	Dimensionality	Space group	Bandgap (eV)	Emission (nm)	Ref.
CsSnBr ₃ film	3	<i>Pnma</i>	—	915	[49]
CsSnI ₃ film	3	<i>Pnma</i>	—	—	[49]
CsSnCl ₃ film	3	<i>Pm3m</i>	—	440	[49]
CsSnI ₃ SCs	3	<i>Pnma</i>	1.31	950	[52]
MASnI ₃ film	3	<i>P4mm</i>	1.3	970	[125]
CsSnCl ₃ NCs	3	<i>Pm3m</i>	2.8	470	[38]
CsSnBr ₃ NCs	3	<i>Pnma</i>	1.8	675	[38]
CsSnI ₃ NCs	3	<i>Pnma</i>	1.3	880	[38]
Cs ₂ SnCl ₆ powder	0	<i>Pm3m</i>	4.6	—	[136]
Cs ₂ SnI ₆ powder	0	<i>Pm3m</i>	1.32	810	[136]
Cs ₂ SnI ₆ film	0	<i>Pm3m</i>	1.3	—	[139]
Cs ₃ Bi ₂ I ₉ powder	0	<i>P6₃/mmc</i>	1.9	—	[69]
Rb ₃ Bi ₂ I ₉ powder	2	<i>P2₁/n</i>	2.1	—	[69]
Cs ₃ Bi ₂ I ₉ film	0	<i>P6₃/mmc</i>	2.05	674	[70]
Cs ₃ Bi ₂ Br ₉ film	2	<i>Pm</i>	2.23	470	[70]
Cs ₃ Bi ₂ Cl ₉ SCs	1	<i>Pnma</i>	2.09	—	[71]
(NH ₄) ₃ Bi ₂ I ₉ SCs	2	<i>P2₁/n</i>	1.46	—	[72]
Cs ₃ Bi ₂ I ₉ QDs	0	<i>P6₃/mmc</i>	—	393	[75]
Cs ₃ Bi ₂ Br ₉ QDs	0	<i>P6₃/mmc</i>	—	410	[75]
Cs ₃ Bi ₂ Cl ₉ QDs	0	<i>P6₃/mmc</i>	—	545	[75]
Cs ₃ Sb ₂ I ₉ NCs	2	<i>Pm1</i>	2.36	580	[86]
Cs ₃ Sb ₂ Br ₉ NCs	2	<i>Pm1</i>	—	410	[87]
Rb ₃ Sb ₂ I ₉ powder	2	<i>P1c1</i>	1.98	—	[85]
Rb ₃ Sb ₂ I ₉ NCs	2	<i>P2₁/n</i>	1.95	630	[88]
Cs ₂ AgBiCl ₆ SCs	3	<i>Pm3m</i>	2.77	—	[53]
Cs ₂ AgBiBr ₆ SCs	3	<i>Pm3m</i>	2.07	685	[54]
Cs ₂ AgBiBr ₆ NCs	3	<i>Pm3m</i>	1.97	650	[57]
Cs ₂ AgInCl ₆ SCs	3	<i>Pm3m</i>	3.3	585	[61]
Cs ₂ AgInCl ₆ SCs	3	<i>Pm3m</i>	3.23	635	[40]
Cs ₂ NaInCl ₆ SCs	3	<i>Pm3m</i>	4.55	—	[64]

structure of the anatase phase was more compatible with MASnI₃ [126]. Gao *et al.* [127] prepared a MASnI₃ film containing lead thiocyanate additives, which significantly improved the film morphology. The absorption edge of the film was located at 950 nm, and the corresponding device exhibited a PCE of 6.03%. The {en}FASnI₃ hollow structure, with randomly distributed Schottky defects and significantly increased bandgap and stability, was produced by incorporating ethylenediamine (en) to FASnI₃. The corresponding device achieved a PCE of 7.14% [128]. A mixture of FA⁺ and MA⁺ cations also effectively improved film morphology and reduced carrier recombination. An FA_{0.75}MA_{0.25}SnCl₃-based device

containing a SnF₂ additive exhibited a PCE of 8.12% [129]. In 2018, Jokar *et al.* [130] reduced the number of tin vacancies in FASnI₃ by introducing bromide, considerably increasing the open-circuit voltage (V_{oc}) and fill factor (FF) of the fabricated solar cell; a PCE of 5.5% was reported. Ran *et al.* [131] produced FASnI₃ thin films with significantly improved uniformity and surface coverage, obtaining optoelectronic devices with a PCE of 6.98%. Liu *et al.* [132] reported a pretreatment method to fabricate a FASnI₃ film by spin-coating a solution of *n*-propylammonium iodide (PAI) in a mixed chloroform/DMSO solvent. DMSO dissolved the surface crystals, creating a liquid-phase environment, while the large PAI

Figure 12 (a) Absorption spectra for MASn_xPb_{1-x}I₃. Reprinted with permission from Ref. [119]. Copyright 2014, the American Chemical Society. (b) Schematic energy level diagram for MASn_xPb_{1-x}I₃ solid-solution perovskites. Reprinted with permission from Ref. [120]. Copyright 2014, the American Chemical Society. (c) *J*-*V* curves for MAPb_{1-x}Sn_xI_{2.6}Br_{0.4} PSCs. Reprinted with permission from Ref. [122]. Copyright 2018, Elsevier. (d) *J*-*V* curves for CsSnI_{3-x}Br_x (0 ≤ *x* ≤ 3) PSCs. Reprinted with permission from Ref. [133]. Copyright 2015, the American Chemical Society. (e) *J*-*V* curves for CsSnBr₃ PSCs containing a SnF₂ additive. (f) *J*-*V* curves for CsSnBr₃ PSCs with no SnF₂. (e) and (f) are reprinted with permission from Ref. [134]. Copyright 2016, the American Chemical Society. (g) *J*-*V* curves for MA₃Bi₂I₉Cl_x, MA₃Bi₂I₉, and Cs₃Bi₂I₉ solar cells. (h) Incident photon-to-electron conversion efficiency (IPCE) curves for MA₃Bi₂I₉Cl_x, MA₃Bi₂I₉, and Cs₃Bi₂I₉ solar cells. (g) and (h) are reprinted with permission from Ref. [99]. Copyright 2015, Wiley.

cations surrounded the FASnI₃ nuclei to form a template. Therefore, a highly crystallized and smooth FASnI₃ film with a low defect density was formed. The corresponding device exhibited a stabilized efficiency of 11.22%, among the highest reported for lead-free PSCs.

Sabba *et al.* [133] successfully improved the *V*_{oc} and *J*_{sc} values of the corresponding device by adjusting the ratios of I and Br in CsSnI_{3-x}Br_x. As the Br content increased, the number of Sn vacancies gradually decreased, and the device output voltage gradually increased (Fig. 12d). Using SnF₂ additive reduced the Sn vacancy concentration in CsSnI₃, with the corresponding device exhibiting a PCE of 2% and significantly improved stability (Fig. 12e and f) [134]. Lee *et al.* [135] obtained a PCE of 2.1% for Cs₂SnI₄Br₂ perovskite devices prepared using a two-step method. Zhu *et al.* [136] controlled the relative content of I⁻/Cl⁻ in Cs₂SnI_xCl_{6-x}, such that the band gap was easily adjusted. The efficiency of planar Cs₂SnI₆ PSCs prepared by Qiu *et al.* [137] was close to 1%, and they demonstrated excellent stability after one week. The efficiency of Cs₂SnI₆-based PSCs employing pulsed laser-deposited ZnO nanorods as the electron transport material was close to 1%. The nanorods adsorbed a larger amount of Cs₂SnI₆, improving the morphology of the film and in-

hibiting charge recombination [138]. A Cs₂SnI₆ film with a pure crystal phase was prepared using aerosol-assisted CVD (AACVD). The film presented a bandgap of 1.3 eV and a uniform morphology. In this process, SnI₄ vapor prevented the decomposition of Cs₂SnI₆, thereby improving the film stability [139].

Double perovskite solar cells

In 2017, Wu *et al.* [140] prepared stable Cs₂AgBiBr₆ thin films through spin-coating and low-pressure-assisted annealing. A planar heterojunction solar cell based on this thin film showed a PCE of 1.44%. Ning *et al.* [141] determined that excitons and free carriers in Cs₂AgBiBr₆ possessed a diffusion length of 110 nm. Gao *et al.* [142] added isopropanol during the spin-coating of Cs₂AgBiBr₆ thin films and combined this with high-temperature annealing to prepare thin films with smooth surfaces and large grain sizes. Solar cells based on an inverted planar heterojunction showed a PCE of 2.23%. Igbari *et al.* [143] compared Cs₂AgBiBr₆ films prepared by either vacuum sublimation or solution methods. The authors observed that the solution-treated films exhibited higher crystallinity, narrower electronic bandgap, longer light excitation lifetimes, and higher mobility. The resulting solar cell

presented an optimized PCE of 2.51%. Various other techniques, such as high-pressure evaporation deposition [144] and metal doping, have been utilized to improve thin-film crystallization quality. When Rb^+ was doped in $\text{Cs}_2\text{AgBiBr}_6$ to form $(\text{Cs}_{1-x}\text{Rb}_x)_2\text{AgBiBr}_6$, light absorption in the long-wavelength region was enhanced, and the defect state density was reduced without changing the crystal lattice. When $\text{Cs}:\text{Rb} = 9:1$, the average PCE of the device was 15 times higher than that of the undoped device [145]. Changing the device structure can also improve the efficiency. Pantaler *et al.* [146] deposited a $\text{Cs}_2\text{AgBiBr}_6$ film on mesoporous TiO_2 , allowing the uniform and compact growth of the perovskite and increasing its contact area with TiO_2 .

Although extensive research has been performed on the $\text{Cs}_2\text{AgBiBr}_6$ double perovskite, the performance of $\text{Cs}_2\text{AgBiBr}_6$ PSCs is substantially inferior to that of devices using lead-based perovskites. Studies have shown that the electron diffusion length in $\text{Cs}_2\text{AgBiBr}_6$ is shorter than the hole diffusion length. The high electron trap density was the major reason for these carrier diffusion lengths [147]. These challenges must be overcome in future studies.

Bi, Sb(III)-based perovskite solar cells

Park *et al.* [99] successfully fabricated zero-dimensional $\text{A}_3\text{Bi}_2\text{I}_9$ ($\text{A} = \text{MA}$ or Cs) perovskites and integrated them in photovoltaic devices. The bandgaps of $\text{MA}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{I}_9$, and $\text{MA}_3\text{Bi}_2\text{I}_{9-x}\text{Cl}_x$ were approximately 2.1, 2.2, and 2.4 eV, respectively. $\text{Cs}_3\text{Bi}_2\text{I}_9$ -based solar cells exhibited PCEs exceeding 1% (Fig. 12g and h). Shin *et al.*

[148] developed a solvent engineering method to prepare dense $\text{A}_3\text{Bi}_2\text{I}_9$ ($\text{A} = \text{MA}^+$, Cs^+ , or FA^+) thin films. $\text{MA}_3\text{Bi}_2\text{I}_9$ -based devices presented the highest PCE of 0.71%. Jain *et al.* [149] exposed a BiI_3 film to MAI steam by a steam-assisted solution process. The best reported PCE of the highly stable $\text{MA}_3\text{Bi}_2\text{I}_9$ -based devices was 3.17%. Saparov *et al.* [81] prepared a $\text{Cs}_3\text{Sb}_2\text{I}_9$ film using a two-step deposition method. This film exhibited a bandgap width of only 2.05 eV. Comparison of the stabilities of $\text{Cs}_3\text{Sb}_2\text{I}_9$ and MAPbI_3 under identical conditions revealed that $\text{Cs}_3\text{Sb}_2\text{I}_9$ decomposed and produced small amounts of CsI over 60 days, while MAPbI_3 decomposed drastically in two weeks. The various performance parameters of lead-free PSCs are listed in Table 2.

LEDs

Materials used in light-emitting and photovoltaic devices require different design principles. Light-emitting devices must have effective exciton recombination through radiation pathways, while the effective separation of excitons is essential for effective photoelectric conversion in solar cell devices. Therefore, luminescent metal halide perovskites exhibiting quantum confinement are suitable for use in light-emitting devices. Owing to the higher probability of exciton recombination in a confined structure, large exciton binding energies can be obtained. Hence, nano-sized perovskites can show higher PLQYs than expected. Two different optical processes are used as guidelines to manufacture efficient light-emitting devices based on emissive materials [150]. One process is PL; PL-based devices employ a separate high-energy light source

Table 2 Parameters of lead-free PSCs

	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	Ref.
$\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$	20.04	0.42	0.5	4.18	[119]
$\text{MAPb}_{0.4}\text{Sn}_{0.6}\text{I}_{2.6}\text{Br}_{0.4}$	23.38	0.80	0.72	13.40	[122]
MASnI_3	15.18	0.72	0.50	5.44	[124]
MASnI_3	17.03	0.54	0.66	6.03	[127]
$\{\text{en}\}\text{FASnI}_3$	22.54	0.48	0.66	7.14	[128]
$\text{FA}_{0.75}\text{MA}_{0.25}\text{SnI}_3$	21.2	0.61	0.63	8.12	[129]
FASnI_3	20.7	0.47	0.74	6.98	[131]
CsSnI_2Br	15.6	0.29	0.38	1.67	[133]
$\text{Cs}_2\text{SnI}_4\text{Br}_2$	6.22	0.56	0.57	2.03	[135]
Cs_2SnI_6	5.41	0.51	0.35	0.96	[137]
FASnI_3	22.10	0.72	0.73	11.2	[132]
$\text{MA}_3\text{Bi}_2\text{I}_9$	4.2	1.01	0.78	3.17	[149]
$\text{Cs}_3\text{Bi}_2\text{I}_9$	2.15	0.85	0.6	1.09	[99]
$\text{Cs}_2\text{AgBiBr}_6$	3.82	1.01	0.65	2.51	[143]

Figure 13 (a) Photo and electrical excitation of perovskite materials. Reprinted with permission from Ref. [150]. Copyright 2018, Wiley. (b) EL spectrum for a white LED (w-LED) combining Cs₃Bi₂Br₉ QDs and the rare-earth phosphor YAG. Insets: digital images of QDs/silica composite devices combined with YAG (off and on). (c) Commission internationale de l'éclairage (CIE) color coordinates for Cs₃Bi₂Br₉ QDs, YAG, and the W-LED device. (b) and (c) are reprinted with permission from Ref. [75]. Copyright 2018, Wiley. (d) Device structure of the (PEA)₂SnI₄ perovskite LEDs. (e) Energy levels for a (PEA)₂SnI₄ perovskite LEDs. (d) and (e) are reprinted with permission from Ref. [93]. Copyright 2017, the American Chemical Society. (f) Current density (black) and brightness (red) as a function of the voltage for a (OAm)₂SnBr₄ perovskite LED. Reprinted with permission from Ref. [94]. Copyright 2018, the American Chemical Society.

for photoexcitation, with energy corresponding to the optical bandgap of the emissive material. The second process is electroluminescence (EL); electrons and holes are injected from the cathode and anode, respectively, into the functional layer under an external electric field, and energy is released from the active layer as luminescence (Fig. 13a). Tang's group [75] prepared Cs₃Bi₂X₉ NCs with a PL peak at 410 nm (FWHM = 48 nm) and a PLQY of 19.4%. The crystal surface was passivated by a BiOBr layer, providing superior water stability. The NCs were mixed with the yellow-emitting rare-earth phosphor Y₃Al₅O₁₂ (YAG) and coated on an ultraviolet GaN chip. The combination of emission peaks from the Cs₃Bi₂X₉ NCs and YAG produced white emission with good light and thermal stabilities. The color temperature was determined to be 8477.1 K (Fig. 13b and c). Zhang's group [151] prepared CsPb_xMn_{1-x}Cl₃ NCs using Mn²⁺ doping to reduce the toxic Pb²⁺ content. The value of x reached 0.46 and the PL peak of the final product was located at 579 nm, with a PLQY of 54%. By coating the orange-red-emitting CsPb_{0.73}Mn_{0.27}Cl₃ NCs on a GaN LED chip, luminescence from the bottom GaN layer was converted into low-energy luminescence emitted from the perovskite NCs. Stable operation of the device was realized

and a luminous efficiency of 2.21 mW⁻¹ was achieved. Ma's group [152] synthesized zero-dimensional, organic, and lead-free (C₄N₂H₁₄X)₄SnX₆ (X = Br, I) and (C₉NH₂₀)₂SbCl₅ perovskites, in which the metal halide octahedral [SnX₆] and tetrahedral [SbX₅] units were separated by the organic ligands C₄N₂H₁₄X⁺ and C₉NH₂₀⁺. Efficient emission was realized by excited-state recombination in each metal halide polyhedron. A PLQY close to 100% was achieved, and the prepared white phosphor LEDs retained stable brightness and color after continuous operation for 6 h.

The EL process is more efficient than the PL process in light-emitting devices. Haque's group [93] used the two-dimensional (PEA)₂SnI₄ perovskite as a TiO₂ sensitizer to prepare an LED with the structure ITO/PEDOT:PSS/(PEA)₂SnI₄/F8/LiF/Al. This device exhibited an EL peak at 630 nm under the current density of 4.7 mA cm⁻² and achieved a brightness of 0.15 CD m⁻² (Fig. 13d and e). Tan's group [153] prepared an LED device with the structure ITO/PEDOT:PSS/MASnI₃/F8/Ca/Ag, displaying near-infrared EL at 945 nm and an external quantum efficiency of 0.72%. With increasing Br content in MASn(Br_{1-x}I_x)₃, the bandgap increased and the EL of the corresponding LED device was blue-shifted from 945 to

667 nm. Zhang *et al.* [94] synthesized two-dimensional (OAm)₂SnBr₄ perovskite NCs by hot injection. The PLQY values were 88% and 68% for the NCs in solution and film states, respectively, owing to the effective separation of [SnBr₆] octahedra by the OAm⁺ insulation layer. (OAm)₂SnBr₄ was used as the light-emitting layer in an inverted LED, exhibiting a low conduction voltage of 2.2 V and a maximum brightness of 350 CD m⁻², the highest brightness reported to date for lead-free perovskite LEDs (Fig. 13f). Yuan *et al.* [154] used valeric acid (VA) to decrease the crystallization rate of a (PEA)₂SnI₄ perovskite, improving the film morphology. The addition of VA also protected tin from oxidation during film formation. The high-quality film and the reduced Sn⁴⁺ content contributed to the high external quantum efficiency (5%) of the resulting LEDs. The color coordinates of the LEDs were (0.708, 0.292), meeting the Rec. 2100 specification for a red emitter.

X-ray detectors

The absorption of X-ray and the effective conversion of photons to carriers are vital for the application of X-ray detectors. High X-ray sensitivities, large charge-carrier mobilities, long charge-carrier lifetimes (τ), and low defect densities are required for scintillators. Zhang *et al.* [155] fabricated an X-ray detector based on Cs₂AgBiBr₆. In the preparation of single-crystal Cs₂AgBiBr₆, washing with isopropanol during high-temperature annealing inhibited the field-driven ion migration and the formation of surface conduction channels, thereby reducing the resistivity and background current of the device. The sensitivity of the X-ray detector was 316 $\mu\text{C Gy}_{\text{air}}^{-1} \text{cm}^{-2}$ at a voltage of 18 V. Three-dimensional single-crystal perovskites exhibit high mobilities and long carrier diffusion lengths, producing high dark currents when they are used in optoelectronic devices. Moreover, internal ions can migrate easily, particularly under high electric

fields, causing detector instability under working conditions, low device signal-to-noise ratios, and baseline drift [156–158]. The crystal grain defect concentration of perovskite structures can be effectively suppressed by reducing the size [159,160]. Xu *et al.* [161] reported that the layered double perovskite (BA)₂CsAgBiBr₇ (BA⁺ = *n*-butylammonium) exhibited a low number of defects and high resistivity. This perovskite presented excellent X-ray attenuation characteristics, based on its X-ray detector sensitivity of 4.2 $\mu\text{C Gy}_{\text{air}}^{-1} \text{cm}^{-2}$, indicating its excellent potential as an X-ray detector material. Liu *et al.* [162] synthesized large-volume, zero-dimensional inorganic single-crystal MA₃Bi₂I₉ with a high X-ray absorption ($\sim 4.1 \text{ g cm}^{-3}$), and a resistivity of $4.7 \times 10^{10} \Omega \text{ cm}$. A coplanar detector fabricated using MA₃Bi₂I₉ SCs exhibited low dark noise current and excellent X-ray response performance, with a minimum detection limit of 31 nGy s⁻¹ and a high sensitivity of 872 $\mu\text{C Gy}^{-1} \text{cm}^2$. Tie *et al.* [163] reported that polycrystalline MA₃Bi₂I₉ presented a high resistivity and a low dark carrier concentration. The low limit of detection (LoD) of the MA₃Bi₂I₉-polycrystalline pellet detector was 9.3 nGy_{air} s⁻¹, with a detection efficiency (28.8%) higher than that of MAPbBr₃ SCs (16.4%) (Fig. 14a). The inorganic zero-dimensional bismuth perovskite is also an ideal material for X-ray detectors. Centimeter-sized Cs₃Bi₂I₉ SCs [101] exhibited low defect density, low trap density, extremely low dark-current noise, and high stability. The fabricated single-crystal Cs₃Bi₂I₉ perovskite X-ray detector showed a high light response with an on/off ratio exceeding 10³ and a high detection rate (10¹² Jones). Low-temperature-grown (NH₄)₃Bi₂I₉ SCs could be sheared along the cleavage plane. An obvious anisotropic X-ray response was observed in (NH₄)₃Bi₂I₉ owing to parallel charge transport and collection anisotropy. The perpendicularly structured device exhibited a greater sensitivity than the parallelly structured device (Fig. 14b and c) [73].

Figure 14 (a) X-ray dose-rate-dependent signal-to-noise ratio (SNR) of a detection device under an electric field of 700 V cm⁻¹. Reprinted with permission from Ref. [163]. Copyright 2020, Wiley. (b) Illustration of parallel and perpendicular device structures. (c) Sensitivities of devices parallel and perpendicular to the (001) surface. (b) and (c) are reprinted with permission from Ref. [73]. Copyright 2019, Springer Nature.

CONCLUSIONS AND OUTLOOK

In recent years, great progress has been made in the development of suitable lead-free alternative perovskites to address the toxicity of lead. Three aspects of Sn-, Bi-, Sb-based, and double perovskites were discussed in this review: growth methods, photoelectric properties, and device applications. The growth methods for lead-free perovskites were similar to those employed for lead-based perovskites. Various forms of lead-free perovskites can be synthesized using solution methods, solid-state reactions, and CVD. Each growth method has its advantages and disadvantages, and a suitable method should be selected according to the material requirements. For example, the anti-solvent method allows the synthesis of high-quality single-crystal Bi-based perovskites; however, the size of the synthesized QDs is uneven and the QDs are easily aggregated. The hot injection method is a more suitable choice to synthesize uniformly sized QDs.

The atomic radius and the arrangement of electron orbitals significantly influence the selection of alternative perovskite elements. The different valence states of an element and the different structures of a single valence state are also important factors governing the photoelectric properties of the material. For example, Sn(II)- and Sn(IV)-based perovskites present two different structures; therefore, the electronic structure and optical properties of the perovskites differ. The bandgaps of Sn(II)-based perovskites are generally smaller than those of Sn(IV)-based perovskites, and Sn(IV)-based perovskites are more stable than Sn(II)-based perovskites. $A_3(\text{Bi/Sb})_2X_9$ exhibits two different structures when different A cations and halogen atoms are incorporated, producing distinct energy band structures and carrier dynamics.

We also examined the properties of two reported double perovskites: $\text{Cs}_2\text{AgBiX}_6$ and $\text{Cs}_2\text{AgInX}_6$. Using these as examples, we discussed the methods to optimize the properties of lead-free perovskites, such as halogen substitution, metal element doping, energy band engineering, and adjusting the structure dimensions.

Finally, the applications of lead-free perovskites in solar cells, LEDs, and X-ray detectors were reviewed. To date, the conversion efficiency of Sn(II)-based perovskite photoelectric devices is above 10%, lagging behind that of lead-based perovskites. The major reason for this is that Sn(II) can be easily oxidized to Sn(IV), causing p-type doping. For LEDs and X-ray detectors, the efficient separation of excitons and the X-ray sensitivity of lead-free perovskites are important research directions.

In future, research on lead-free perovskite will be

challenging; researchers can focus on the physical and chemical optimization of these materials to approach the excellent properties of lead-based perovskites. It is also important to study the unique properties of lead-free perovskites that are different from those of lead-based perovskites, and to expand their application scope.

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Fan Yang received her bachelor's degree (2018) from Liaoning University. She is now pursuing a master's degree at Tianjin University. Since June 2019 she has been a joint student at the National Center for Nanoscience and Technology (NCNST) under the supervision of Prof. Xinfeng Liu. Her research interests focus on the growth and optical properties of single-crystal perovskites.

Shaoli Wang received her PhD degree from the Institute of Chemistry, Chinese Academic Sciences in 2014. Then she joined the Experiment Center of Forestry in North China of the Chinese Academy of Forestry and engaged in material-related scientific research. At the end of August 2019, she joined the research group of Xinfeng Liu at the NCNST. Her research interests focus on new nano materials.

Xiaotao Zhang is an associate research fellow of Tianjin University. He received his PhD degree from the Institute of Chemistry, Chinese Academy of Sciences in 2012. Then he worked at the same institute as a postdoctoral fellow. Since 2015, he has been working as an associate research fellow at Tianjin University. His research group mainly focuses on the preparation of organic cocrystals and devices, organic optoelectronic materials, and the printing of thin film and flexible devices.

Xinfeng Liu is a professor at the NCNST in China. He received his PhD in 2011 at the NCNST. Then he joined the School of Physical and Mathematical Sciences of Nanyang Technological University, Singapore, as a postdoctoral fellow. He joined the "100-Talents" Program of the Chinese Academy of Sciences in 2015 and then became a professor at the NCNST. His research group mainly focuses on light-matter interactions and ultrafast spectroscopy at the micro-/nano-scale.

非铅钙钛矿的合成、性质和应用

杨凡^{1,2}, 王傲成^{1,2}, 岳帅^{2,3}, 杜文娜^{2,3}, 王少丽^{2,4*}, 张小涛^{1*}, 刘新凤^{2,3*}

摘要 卤化铅钙钛矿由于具有高吸收系数、高载流子迁移率、高缺陷容忍度和高光致发光效率等优异的光电子性能, 近年来引起了人们的广泛关注. 然而, 阻碍其广泛应用的一个关键问题是铅元素引起的毒性. 为了解决这一问题, 使用其他无毒元素替代铅是一个很有前途的研究方向. 在综合考虑原子半径、相对原子质量、电子排布等条件下, 以锡、铋、锑等元素代替铅的类钙钛矿已被广泛合成. 本文从制备方法、光电性质、器件应用等几个方面综述了这几类非铅基钙钛矿. 首先, 介绍了非铅基钙钛矿主要的制备方法: 溶液法、固相反应法和化学气相沉积法; 其次, 从不同结构维度讨论了非铅基钙钛矿的光电性能及其性能优化方法; 最后, 讨论了非铅基钙钛矿在太阳能电池、发光二极管和X射线探测器中的应用. 希望本综述能给未来非铅钙钛矿的研究和发展提供一定的参考价值.