Emerging new-generation white light-emitting diodes based on luminescent lead-free halide perovskites and perovskite derivatives

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Abstract
Phosphor-converting white light-emitting diodes (WLEDs) are promising and particularly appealing solid-state light sources, which are expected to change the way we light our homes and businesses. Lead-halide perovskites have recently received extensive research attention as a new class of phosphors in WLEDs owing to their high photoluminescence quantum yield, tunable fluorescence emission, and the facile processing technique. However, the stability issues and the lead toxicity of such perovskites severely restrict their commercialization and practical applications. In this review, we first present a discussion on the recently developed luminescent lead-free halide perovskites and perovskite derivatives by discussing their various design routes and emission mechanisms. Second, we introduce and compare three types of phosphor-converting WLEDs with different cell configurations, and then discuss the recent advances and limitations in WLEDs based on lead-free metal-halide materials. Finally, we highlight current existing challenges and future development directions for developing high-performance WLEDs.

KEYWORDS
lead-free, perovskites, phosphors, photoluminescence, white light-emitting diodes

1 | INTRODUCTION

Compared with the conventional fluorescent lamps and incandescent bulbs, phosphor-converting white light-emitting diodes (WLEDs) can economize at least 80% electrical energy and possess 25 times working lifetime.\cite{1-3} Thus, it is one of the most energy-saving and rapidest-growing technologies in the world for the lighting and displays.\cite{4,5} Currently, the commercial WLEDs are fabricated by combining blue-emissive LED chips with yellow-emissive phosphors or a mixture of green and red phosphors.\cite{6,7} However, almost all the commercial phosphors contain rare-earth elements, such as Eu$^{2+}$, Tb$^{3+}$, or Ce$^{3+}$, and their potential price raises and supply risks are barriers for future large-scale application and commercialization.\cite{8} One of the solutions is to develop...
a new-generation of light emitters that could overcome the shortcomings of existing commercially phosphors. As a possible alternative, organic polymers suffer from continuously luminescence degradation under high temperature, and their low color purity results in a poor white light quality. Colloidal quantum dots (QDs) possess improved color purity, but the high reaction temperature and complicated synthetic processes (delicate surface passivation or shellling) restrict their mass production and increase the preparation cost. Under this circumstance, exploring low-cost, color-stable, and easy-to-synthesize light emitters is certainly a promising research subject.

Recently, metal-halide perovskites have attracted great research interest as highly promising light emitters in phosphors-converting WLEDs because of their excellent luminescence properties, such as tunable fluorescence emission, high color purity, wide color gamut, and near-unity photoluminescence quantum yield (PLQY). Another important advantage is that they could be synthesized by a variety of different processing techniques, such as solid-state reaction, solution method, vacuum-evaporation technology, and especially the facile low-temperature solution processing technique that makes the perovskite light emitters more attractive. In 2015, Snaith and colleagues pioneered a strategy for low-cost white light sources by using perovskites as the down-converters. Since then, the progress of this strategy has been vivifying in the past 5 years. Despite the rapid advances achieved in perovskite WLEDs, the practical industrialization of these emerging technologies still suffers from two thorny issues, namely the well-known Pb toxicity and poor materials stability against environment moisture/oxygen, ultraviolet (UV) light, and heat. These issues have motivated researchers to develop strategies to search environmentally stable and lead-free perovskites. At present, tremendous theoretical and experimental efforts have been devoted to screen suitable perovskites, and some promising candidates have been identified. To this end, several equivalent and heterovalent substitution concepts have been proposed to replace Pb with Sn(II), Sn(IV), Bi(III), Sb(III), Cu(I), Ag(I), and In(III) in perovskite lattices, and the resulting products exhibit many attracting features, such as a low toxicity, an improved stability, and an also efficient emission, thus facilitating their applications in WLEDs. However, from the application point of view, there is still a long way to go because a reliable white light source should be characterized by a high luminous efficiency, a brilliant color-rendering property, a high color stability, and a long operation lifetime that depend strongly on the performance of emissive components. Therefore, an intensive and comprehensive study on the nature and limitations of lead-free candidates and the factors that dominate the general trends of WLEDs is crucial for promoting the technological applications.

2 | DESIGN ROUTES OF THE LUMINESCENT LEAD-FREE PEROVSKITES AND PEROVSKITE DERIVATIVES

Generally, metal-halide perovskites contain a chemical formula of ABX₃, where A represents monovalent organic/inorganic cations (e.g., CH₃NH₃⁺ (MA), CH(NH₂)₂⁺ (FA), Cs⁺ or Rb⁺), B is a divalent lead cation (Pb²⁺), and X is a halogen anion (e.g., Cl⁻, Br⁻, I⁻). According to the general perception, the divalent cations of group-14 element, such as Sn²⁺ and Ge²⁺, are appropriate alternatives for substituting the toxic Pb²⁺ in the traditional perovskite structure, because they both meet the prerequisites for coordination and charge balance. The comparable ionic radius (e.g., Sn²⁺, 1.35 Å; Pb²⁺, 1.49 Å) and same valence also avoid the major alterations caused by the substitution. However, it should be considered that the divalent Sn²⁺ ions provide the possibility of oxidation (Sn⁴⁺), resulting in high defects density. In contrast, the perovskite derivatives obtained by direct use of Sn⁴⁺ shows much higher stability due to the stable +4 oxidation state. The crystal structure of A₂B⁺⁴X₆ with stable oxidation state is characterized by a typical zero-dimensional structure, featuring [BX₆]²⁻ octahedra isolated by the A⁺ cations, which may provide quantum confinement and improve the PLQY. In addition, when searching for elements to replace Pb in halide perovskites, the high defect tolerance is one of the essential considerations. To obtain high defect tolerance, the conduction band minimum has to be stabilized by spin-orbit coupling, and the valence band maximum must exhibit antibonding characteristics. These electronic properties depend on the two electrons in the outermost s orbital of Pb²⁺ (6s²). Encouragingly, trivalent Bi⁵⁺ and Sb³⁺ with less toxicity share the ns² electronic configuration with Pb²⁺, and therefore are expected to replace the lead elements in perovskites. Moreover, due to the high trivalent oxidation states for Bi⁵⁺ and Sb³⁺, the resulting A₃B³⁺²X₉
configuration becomes the stable stoichiometry. Notably, Goldschmidt tolerance factor ($t$) and octahedral factor ($\mu$) are two important parameters to evaluate the perovskite phase formability and stability.\[31\] According to the limitation of ionic radii on the involved cations and anions, the stability and formability range for perovskite structure can be deduced to be $0.81 \leq t \leq 1.1$ and $0.44 \leq \mu \leq 0.90$. Theoretical calculations suggest that most of the class of double perovskites possess a stable three-dimensional cubic structure, which is consistent with the successful experimental preparation.\[37\] Also, the halide double perovskites can offer great opportunities in terms of combinatorial chemistry due to their rich ion selectivity. It is worth mentioning that the type of bandgap (direct or indirect) is also an important determining factor for efficient light emission.\[24\] For direct bandgap materials, the absorption and recombination process involves only photons, which ensures a fast radiative recombination of charge carriers. More recently, a series of novel ternary copper halides with direct bandgap properties have been extensively studied, and their excellent emission performances are almost comparable to the Pb-based counterparts.\[36\] Figure 1 summarizes all possible substitution candidates along with their crystal structures and the chemical compositions, and the advantages and disadvantages of each group of materials are also provided. At present, lead-free perovskites and their derivatives still need to be further explored, and the theoretical and experimental efforts on material design should be enhanced.

**FIGURE 1** Possible candidates for lead-free perovskites and perovskite derivatives along with their crystal structure

3 | PL MECHANISM IN LUMINESCENT LEAD-FREE PEROVSKITES AND PEROVSKITES DERIVATIVES

To explore the potential of lead-free metal-halide materials as the phosphors, it is very necessary to understand their PL mechanism and study the factors that influence their emission properties.\[34\] In comparison to the Pb-based perovskites, lead-free metal-halide perovskites show several particular emission properties, which will be discussed in this section. The typical band-to-band transition for light generation generally shows a narrow full-width at half-maximum (FWHM), small Stokes shifts, and lifetimes on the order of nanoseconds.\[35\] The corresponding photophysical model can be briefly described as follows: electrons transit from the ground state to the excited state under light excitation, and meanwhile, generating holes in the ground state.\[28\] Subsequently, the electrons and holes recombine radiatively to emit photons, as shown in Figure 2A. Among the lead-free perovskite systems, Sn$^{2+}$- and Ge$^{2+}$-based perovskites (CsSnX$_3$ and CsGeX$_3$), are typical band-to-band transition luminescent material. Such a narrow emission has significance in enhancing the imaging contrast with minimal background noise and increasing the high color-purity displays. There is no doubt that good color-rendering white light can be obtained by a combination of narrow emitting materials with two or more colors, such as that observed in reported lead-based perovskites.\[23–25\] Moreover, quasi-two-dimensional
perovskites with multiphase structure are emerging as efficient luminescent materials for highly performed lighting devices due to the cascade energy landscape for efficient exciton transfer and the subsequent radiative recombination, as shown in Figure 2B. Such luminescence structure is common in lead-based perovskites, but is rare in lead-free perovskite systems, and can only be observed in Sn$^{2+}$-based perovskites. Chiu et al. investigated the influence of a series of organic ammonium cations on the luminescence characteristics of Sn$^{2+}$-based perovskites (Figure 2C), and demonstrated that a large dielectric contrast between the organic cations and the tin iodide layer can greatly improve the PLQY. Unlike the typical narrow emission in lead-based perovskites, the majority of lead-free perovskites and their derivatives exhibit a broadband emission with large FWHM and large Stokes shifts. This unusual broadband emission is attributed to the self-trapped excitons (STEs)-related radiative recombination, which has been demonstrated by many researchers.

Such STEs are regarded as the electron-hole pairs immobilized in “excited-state defects,” which result from the transient elastic lattice distortions. In the self-trapping process of STEs, the collective effect of energy loss of the self-trapping energy ($E_{st}$), lattice deformation energy ($E_d$) and the exciton binding energy ($E_b$) result in a large Stokes shift in STEs emission, as shown in Figure 2D. It is worth noting that the STEs emission is fundamentally different from the intrinsic defect emission due to the distinct origins of lattice defects. Specifically, the ground state of STEs has a perfect lattice structure, and the transient lattice distortion occurs only in light excitation, as shown in the top of Figure 2E. In contrast, the crystal lattice of materials with permanent defect emission or doping impurity ions emission is inherently imperfect (middle and bottom of Figure 2E), and thus the excitons are easily trapped by these low-energy intrinsic defect states, and their emission intensity is closely related to the number of defects. Besides, the strong electron–phonon coupling and soft crystal lattice are another two key essentials for STEs formation, which promote the strong elastic deformation of the excited state lattice. The electron–phonon coupling is closely related to the FWHM of PL spectrum, which is usually evaluated by the Huang-Rhys factor ($S$) obtained from the temperature-dependent PL results, as seen in Tang’s study on Cs$_2$AgInCl$_6$ (Figure 2F). A general consensus is that $S$ is proportional to...
the possibility of STEs formation together with the value of FWHM. However, an excessively large $S$ will increase the possibility of nonradiative recombination, which is not conductive to the efficient STEs emission.\cite{22} In addition, the transient absorption spectroscopy can identify the STE recombination process, which provides direct evidence for the existence of STEs.\cite{35} It is believed that the formation of STEs has a strong relationship with the dimensionality of materials system. In other words, the low crystal dimensionality could facilitate the octahedral distortion and STEs formation due to the soft and deformable lattice nature, usually observed in low-dimensional lead-free perovskites.\cite{36} For lead-free perovskite phosphors, the broadband emission from STEs can cover most visible region and the large Stokes shift can reduce the photon self-absorption, which is beneficial for WLEDs construction. However, too large Stokes shift would also lead to the increase of excitation energy, making it difficult to achieve a high luminous efficiency.\cite{22} Therefore, optimizing the excitation wavelength is necessary for the phosphors emitted by STEs, which can be achieved by exploring the other element alloying or substitution to minimize the lattice deformation energy and self-trapping energy.

**4 | WLED DEVICE CONFIGURATION**

A well-known and common way of WLED configuration is to combine a blue-emissive chip with a yellow-emissive phosphor, as shown in Figure 3A. In this process, the phosphor emits yellow light under the excitation of blue chips, and the white light is generated when blue and yellow light are mixed.\cite{38,39} However, this approach lacks the green and red light contributions and results in a high correlated color temperature (CCT) and low a color-rendering index (CRI), which limits their applications for high-quality indoor lighting.\cite{2,3} To overcome the above problems, the three primary colors of red, green, and blue (RGB) phosphors can be introduced into the conversion layer on the UV chips to expand the white region of the spectral emission (Figure 3B). This multi-component based WLED structure can produce good color-rendering properties, close to the standard white light with Commission International de l’Eclairage (CIE) coordinates of (0.33, 0.33).\cite{7} In 2015, Snaith et al. fabricated the first perovskite WLED using a multi-component structure, where the blending multi-color MAPbX$_3$ ($X = \text{Cl, Br, and I}$) phosphors were excited by a blue GaN chip.\cite{13} Thanks to the highly tunable emission and high PLQY over the entire visible spectrum, the luminous efficiency of this type of WLEDs achieved a value of 109 lm W$^{-1}$.\cite{11} Nonetheless, there are still several inevitable drawbacks for such multi-component strategy, such as a complicated device processing with increased cost, an efficiency losses arising from the emission color changes due to different degradation rates of the phosphors, and an undesired photon self-absorption.\cite{8} Therefore, a highly promising strategy is to achieve a single-component phosphor with the broadband white light emitting feature that can be excited by a UV LED (Figure 3C), which can address the color separation and color instability issues of the blended phosphors. Typically, Tang et al. reported broadband emissive sodium-doped Cs$_2$AgInCl$_6$ double perovskites with a high PLQY of 86% and an impressive stability against UV light and heat, which stimulates intensive researches on the single-component lead-free phosphors.\cite{40} However, the UV chips used in single-component WLEDs generally suffer much a lower efficiency than the blue chips, which results in a low luminous efficiency of the resulting WLEDs.\cite{41} For this purpose, a combination of a broadband emission in the green-red region and a blue chip might be the best compromise to obtain a good color quality as well as a high luminous efficiency.
5 | LEAD-FREE METAL-HALIDE MATERIALS-BASED WLEDs

For phosphor-converting WLEDs, in addition to considering the basic device configuration, ideal down-conversion phosphors are considered to be the key and technologically important components for white light generation. Encouragingly, many efforts have been devoted to develop various lead-free perovskite materials with high luminescence, broadband emission, and large Stokes shift, which make them a promising candidate for WLED applications. In this section, several notable achievements of WLEDs based on different kinds of lead-free candidates in the last few years are classified and discussed.

5.1 | Sn-based perovskites for phosphor-converting WLEDs

The group-14 element Sn(II) is first explored as a candidate to replace Pb because they have the same valence and similar electronic structure. However, the thermodynamically favored Sn$^{4+}$ makes oxidation a critical stability drawback for Sn(II)-based perovskites and devices. To obtain the air-stable Sn-based perovskites, organic long chains were used to reduce the structural dimension during synthesis. For instance, Ma and colleagues first reported an air-stable zero-dimensional (C$_4$N$_2$H$_{14}$Br)$_4$SnX$_6$ (X = Br, I) perovskite, showing an intrinsic broadband yellow emission with a PLQY of close to unity. Phosphors-converting WLEDs using yellow-emissive (C$_4$N$_2$H$_{14}$Br)$_4$SnBr$_6$ perovskites and commercial blue-emissive BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphors as down-converters showed the CIE coordinates of (0.36, 0.37), a CRI value of 70, and a CCT of 4946 K. The fabricated WLEDs also exhibited decent color stability against varying operating current, as shown in Figure 4B. Because of the absence of green and red components in active layers, the white emission had a low CRI. To address the issues of limited spectral coverage and low CRI, three-color multi-component WLEDs with an optimized CRI of 89 and a CCT of 6530 K were demonstrated by Deng
and co-workers.[49] In addition, a range of “warm” to “cold” white light were obtained by controlling the mixing ratio between the yellow (OCTAm)2SnBr4 and commercial blue/green phosphors, as shown in Figure 4C, corresponding to the CIE coordinates ranging from (0.48, 0.41) to (0.33, 0.31) and CCT ranging from 2500 to 6530 K (Figure 4D). Similarly, Zhou et al. used the (C4N2H14Br)4SnBrxI6 phosphor-converting WLEDs orange-red Cs2SnCl6:0.59% Sb, blue Cs2SnCl6:2.75% Bi, and Li and co-workers demonstrated a WLED by assembling 4486 K was achieved, as shown in Figure 4F. Similarly, solution with a CIE coordinate of (0.36, 0.37) and a CCT of 4486 K was achieved, as shown in Figure 4F. Similarly, the Cs2SnCl6:Bi also demonstrated an impressive thermal and water stability due to the stable oxidation state of Sn(IV) and the formation of BiOCl protective layer encapsulating the luminescent material. As seen in Figure 4E, even after a thermal treatment at 200°C for 30 minutes, only a small emission decay occurs for Cs2SnCl6:Bi. By combining with the yellow phosphors (Ba2Sr2SiO4:Eu2+ and GaAlSiN3:Eu2+), a stable warm white light emission with a CIE coordinate of (0.36, 0.37) and a CCT of 4486 K was achieved, as shown in Figure 4E. Similarly, Li and co-workers demonstrated a WLED by assembling orange-red Cs2SnCl6:0.59%Sb, blue Cs2SnCl6:2.75%Bi, and green Ba2Sr2SiO4:Eu2+ phosphors onto the commercial (Ba, Sr)2SiO4:Eu2+ UV chips, and the maximum CRI reaches 81.[52] Although the recent progresses of lead-free Sn-based perovskites are encouraging, the CRI is still not high, and the device degradation under continuous operation exists. Further efforts into the CRI improvement and device degradation mechanisms for such WLEDs are needed.

5.2 Bi-based perovskites for phosphor-converting WLEDs

Apart from the group-14 element, another possible approach is to replace Pb with adjacent kin elements, such as Bi(III) and Sb(III).[53–63] In 2016, Leng et al. first reported the colloidal synthesis of MA3Bi2X9 (X = Cl, Br, and I) QDs by a facile ligand-assisted recrystallization method.[61] Typically, the as-synthesized MA3Bi2Br9 QDs exhibited the blue emission at ∼423 nm and a better stability than the conventional lead-halide perovskites systems. While, a small PLQY of 12% for the products remains highly unsatisfactory and needs to be improved. It is generally accepted that the residual surface states caused by dangling bonds on the QD surface ought to bear mostly liability for the low PLQY, which are likely to serve as the nonradiative recombination centers.[65] Thus, the defect passivation is considered as an effective method to enhance the PL performance.[58] For example, Tang and co-workers systematically optimized the amount of organic ligands to reduce the surface defects of Cs8Bi2Br9 QDs during the synthesis, and the resulting QDs exhibited an improved PLQY of 19.4% (Figure 5A).[53] The WLEDs, using blue-emissive Cs3Bi2Br9 QDs and yellow-emissive Y3Al5O12:BiOBr nanocomposites to achieve a substantial enhancement of PLQY by ~130%.[54] Due to the passivation effect of the BiOBr matrix, the treated Cs3Bi2Br9 QDs exhibited suppressed residual trap states, and showed a bright blue emission at 410 nm with an improved PLQY of 46.4%, which can be explained by the increased PL lifetime and exciton binding energy according to the temperature-dependent steady-state and time-resolved PL spectra. Thanks to the intrinsic stability and high luminance of treated Cs3Bi2Br9 QDs, they further demonstrated a WLED by combining treated Cs3Bi2Br9 QDs with commercial (Ba, Sr)2SiO4:Eu2+ phosphors (Figure 5C). The CIE color coordinates of the WLEDs were measured to be (0.321, 0.334), close to the optimal white-light positioning, as displayed in Figure 5D. Moreover, the studied device demonstrated a long-term stability, and almost no emission intensity decay was observed for 10 hours operating in ambient air, which is much better than the reference device with conventional blue-emissive CsPbCl1.5Br1.5 QDs as the phosphors (Figures 5E,F). These findings suggest the promising potentials of Bi-based perovskites for WLED applications, but the PLQYs achieved are still far from those of the lead-based perovskites. Therefore, more researches on such materials are required to develop effective methods to improve the PLQYs of them, so that the high-performance phosphor-converting WLEDs would be possible.

5.3 Sb-based perovskites for phosphor-converting WLEDs

Analogous to Bi-based perovskites, the trivalent Sb is iso-electronic with divalent Pb cations and possesses similar electronegativity.[64–70] Therefore, Sb-based halide perovskites are a potential alternative to Pb-based perovskites for light-emitting applications to address the toxicity and environmental stability issues.[71,72] For instance, two organic-inorganic Sb-based halides with specific forms of (TATA)2SbCl5 (TATA = tetraethylammonium) and...
(TEBA)$_2$SbCl$_5$ (TEBA = benzyltriethylammonium) were explored by Li and his colleagues. Both compounds exhibited a dual-band emission with a strong broad low-energy band (i.e., orange emission) and a weak high-energy band (i.e., blue emission), as shown in Figure 6A–D. Temperature-dependent PL and density functional theory modeling indicated that the dual-band emission stems from the radiative recombination from singlet and triplet STEs in inorganic [SbCl$_5$]$_2$– pyramids. Such broadband emission properties with near-unity PLQY enable them to be used as promising down-conversion phosphors for WLEDs preparation. As a result, an UV-excited WLED by using yellow (TEBA)$_2$SbCl$_5$ and blue BaMgAl$_{10}$O$_{17}$:Eu$_{2}^{2+}$ was demonstrated, which showed a bright white light with the CIE coordinates of (0.36, 0.33), a CCT of 4282 K, and a CRI of 82 (Figure 6E,G). Moreover, the fabricated devices showed an excellent color stability when driven at varying currents (Figure 6F). Similarly, Xu et al. reported an intense white-light emission with CIE coordinates of (0.43, 0.34) from organic-inorganic hybrid (C$_{12}$H$_{24}$O$_{6}$)$_2$SbCl$_5$ powders. Considering the volatile nature of organic chains under harsh conditions, more attempts have been implemented to use inorganic cations to realize more stable materials. Zhang et al. reported for the first time the synthesis and optical properties of all-inorganic Cs$_3$Sb$_2$X$_9$ QDs (X = Cl, Br, I) by a modified ligand-assisted reprecipitation strategy. The typical Cs$_3$Sb$_2$Br$_9$ QDs were characterized by a bright blue emission at 410 nm with a high PLQY of 46% and good stability, which suggests that the Cs$_3$Sb$_2$Br$_9$ QDs are a potential down-conversion emitter. In parallel, Song and colleagues reported an all-inorganic Sb-based perovskite nanocrystal, K$_3$SbCl$_6$, with a blue emission centered at 440 nm and a PLQY of 22.3%. By further introducing the Mn$^{2+}$ ions into K$_3$SbCl$_6$, a white light emission with tunable CCT from 8173 to 4779 K and high CRI more than 80 was achieved. More recently, Shi et al. adopted a strategy of directly controlling halide components to prepare full-composition Cs$_3$Sb$_2$X$_9$ QDs without phase separation. The obtained Cs$_3$Sb$_2$X$_9$ QDs with different halide compositions exhibited a regular color change from violet to red, with corresponding emission wavelength ranging from 385 to 640 nm (Figure 6H). Such a good spectral tunability facilitates their applications as multi-color phosphors in lighting and display. Moreover, these QDs have been demonstrated to be stable against UV light irradiation, which is beneficial to the UV-excited devices. When the Cs$_3$Sb$_2$Br$_9$ QDs solutions were exposed to UV light for 73 hours continuous irradiation, the bright
blue emission can still be preserved, while the conventional CsPbBr$_3$ QDs lost most of the luminance, as shown in Figure 6I, J. The significantly different UV light stability of CsPbBr$_3$ and Cs$_3$Sb$_2$Br$_9$ is closely associated with their different structural dimensions. The shortening of Br–Sb–Br bond length and the reduction of distortion angle in the SbBr$_6$ octahedron would reduce the total energy of the system, thus increasing the intrinsic structural stability of Cs$_3$Sb$_2$Br$_9$. Besides, theoretical calculations confirmed that the decomposition energy of trigonal Cs$_3$Sb$_2$Br$_9$ is much higher than that of cubic CsPbBr$_3$, which also implies that the Cs$_3$Sb$_2$Br$_9$ is more stable than CsPbBr$_3$. Moreover, native defect migration in perovskites (i.e., Br vacancy, $V_{\text{Br}}$) was considered to be one of the factors leading to a poor stability. Interestingly, the diffusion barriers of $V_{\text{Br}}$ in Cs$_3$Sb$_2$Br$_9$ were much higher than that in CsPbBr$_3$ in the diffusion paths along the $ab$ plane and $c$ axis. Therefore, we have reasons to believe that the nondiffusion behavior of the dominant defects improves the chemical stability of Cs$_3$Sb$_2$Br$_9$. These observations confirmed theoretically and experimentally that the Sb-based perovskites have higher stability than the
Pb-based counterparts, emphasizing that they are suitable candidates for WLED applications even under harsh conditions.

5.4 In-based perovskites for phosphor-converting WLEDs

Another potential candidate for the substitution of lead in the perovskite structure is the group-13 element Indium.[73–77] In comparison to Pb$^{2+}$, the trivalent In$^{3+}$ has a relatively small atomic volume, and thus this heterovalent substitution tends to form a low-dimensional structure.[78–80] Kuang et al. first reported the zero-dimensional In-based perovskites Cs$_2$InCl$_5$$\cdot$H$_2$O and (C$_6$H$_{14}$N$_2$)$_2$In$_3$Br$_{10}$, which presented red broadband emission with PLQY of 33% and 3%, respectively.[73,74] However, their light absorption coefficient corresponding to the excited region is small, resulting in low PL intensity, similar to the materials with parity forbidden transition, thus limiting their further application. To improve the PL performance of such perovskites, a strategy of doping Sb into Cs$_2$InCl$_5$$\cdot$H$_2$O lattice was proposed by Xia and colleagues,[75] and the resulting Cs$_2$InCl$_5$$\cdot$H$_2$O: 5% Sb$^{3+}$ showed a strong yellow emission with a high PLQY of 95.5%, as seen in Figure 7A,B. The optical characterizations along with the theoretical calculations demonstrated that the characteristic singlet and triplet STE emissions of ns$^2$ metal-halide centers account for the efficient luminescence. Using Cs$_2$InCl$_5$$\cdot$H$_2$O: 5% Sb$^{3+}$ powders as a yellow down-conversion phosphor, a highly bright WLED with the CIE coordinates of (0.36, 0.35), a CCT of 4556 K, and a CRI of 86 was demonstrated (Figure 7C,D). Similarly, Xie et al. reported a Sb-doped (C$_8$NH$_{12}$)$_6$InBr$_9$$\cdot$H$_2$O single crystal, which exhibited a warm white-light emission with a PLQY of 23.36%, a CCT of 3347 K, and a CRI of 84.[76] Later, Chen and co-workers synthesized another In-based (C$_6$H$_3$CH$_2$NH$_3$)$_3$InBr$_6$ perovskite that shows a broadband orange emission with an ultra-large Stokes shift of 245 nm and a FWHM of 132 nm (Figure 7E).[77] The use of such
materials as down-converters has a great potential to overcome the problems observed in the conventional WLEDs based on mixed phosphors, such as the efficiency losses due to self-absorption and the changes of the white light quality over time due to different aging of mixed phosphors. Therefore, the resulting WLEDs based on such perovskites exhibited a stable white light with the CIE coordinates of (0.336, 0.376) and a CRI of 87 (Figure 7F). Although the success of these In-based perovskites in WLEDs applications is surprising, these technologies still rely on the commercial phosphors containing rare-earth elements, which is not good for future large-scale deployment. More efforts in the future should pay more attention to exploring multicolor In-based perovskites to realize rare-earth-free WLEDs technology.

5.5 Double perovskites for phosphor-converting WLEDs

Double perovskites, obtained through the heterovalent replacement of a pair of Pb(II) ions by one monovalent B⁺ and one trivalent B³⁺ ions, also attracted researchers' intensive attention. This type of materials have a general formula of A₂B⁺B³⁺X₆ and can maintain a three-dimensional cubic structure (Figure 8A). Among all of the possible arrangements of A₂B⁺B³⁺X₆, Cs₂AgInCl₆ double perovskite was proposed as one of the promising replacements of conventional lead-based systems owing to its good stability and direct bandgap feature. Manna and co-workers pioneered the synthesis and characterizations of colloidal Cs₂AgInCl₆ QDs with broadband white emission (400-800 nm). Although the single-component white light emission was fascinating, this material suffered from a low PLQY ∼1.6% because of the inversion-symmetry-induced parity-forbidden transition, in other words, dark transition. To solve this critical problem, Tang et al. proposed a strategy of Na alloying into Cs₂AgInCl₆ to break the parity-forbidden transition and reduce the electronic dimensionality, enabling efficient white emission via radiative recombination of STEs. Further, trace amounts of Bi were doped into the lattice to passivate the defects and suppress the nonradiative recombination. By optimizing the Na and Bi contents, a record PLQY of about 86% was achieved (Figure 8B). Moreover, such emission can endure a high temperature of 150°C under a continuous UV light irradiation for 1000 hours, as shown in Figure 8C. Further, an UV-excited WLED based on optimally Cs₂Ag₀.₉Na₀.₁In₀.₃Bi₀.₁Cl₆ phosphors was demonstrated, as shown in Figure 8D, which exhibited a warm white light with the CIE coordinates of (0.396, 0.448) and a CCT of 4054 K, respectively. To enable the solution processing and enrich the application fields of this promising material, Tang et al. further developed the colloidal synthesis of Cs₂Ag₁–ₓNaₓIn₁–ₓBiₓCl₆ (x = 0–1, y = 0.03–0.16) QDs through the recrystallization method. By varying the elemental compositions, the PL and color temperature of QDs can be controlled conveniently, as displayed in Figure 8E. Assisted with Bi³⁺ ions doping and ligand passivation, the PLQY of Cs₂Ag₁–ₓNaₓIn₁–ₓBiₓCl₆ double perovskite nanocrystals exhibited tunable white emission under UV light excitation, by simply increasing the Bi dopant contents. More recently, Shi et al. used the Cs₂Ag₀.₇Na₀.₃InCl₆:Bi materials with improved PL performance as the single-component phosphors, and a high-performance warm-light WLED with the CIE coordinates of (0.38, 0.44), a CCT of 4337 K, and a high CRI of 87.8 was demonstrated (Figures 8F,G). Moreover, the proposed WLEDs exhibited an excellent working stability in air ambient, with only a ~4.5% emission decay after a 1000 hours continuous operation, the longest lifetime for perovskite-based WLEDs as far as we know (Figure 8H). The above results suggest that the lead-free double perovskite systems are potentially an attractive candidate to be applied in WLEDs in virtue of their high PLQY, absent light self-absorption, and intrinsic broadband emission nature. Unfortunately, such single-component strategy for WLEDs always suffers from a low CRI due to the lack of effective green and red light contributions, which limits the applications for color-critical high-level lighting, such as art galleries, jewelry, surgery, and photography.

5.6 Cu-based halides for phosphor-converting WLEDs

More recently, ternary copper halides have been extensively explored as a replacement for Pb-based perovskites in virtue of their low toxicity, low-cost, earth abundance, and high luminescent efficiency. In 2018, Hosono et al. first reported the zero-dimensional ternary copper halides, Cs₃Cu₂I₅, which consists of isolated [Cu₂I₅]³⁻ tetrahedrons surrounded by Cs⁺ ions. It shows a bright blue emission peaked at 445 nm with a large Stokes shift of ~155 nm and high PLQYs of 90% and 60% for single crystals and thin films, respectively (Figure 9A). The emission mechanism of this material could be explained by the structural reorganization of excited-states caused by the Jahn–Teller distortion. Generally, the low-dimensional systems exhibit better structural stability than the three-dimensional phase. Experimental efforts have also confirmed the excellent stability of Cs₃Cu₂I₅.
FIGURE 8  A, Schematic illustration of B⁺/B³⁺ cation substitution from halide perovskites (AB₂X₃) to double perovskites (A₂B²⁺B³⁺X₆). Reproduced with permission [87] Copyright 2018, Royal Society of Chemistry. B, Luminosity function (dashed line) and PL spectra (solid lines) of Cs₂Ag₀.₆₀Na₀.₄₀InCl₆ measured at different temperatures from 233 to 343 K. C, Operational stability of Cs₂Ag₀.₆₀Na₀.₄₀InCl₆ down-conversion devices, measured in air without any encapsulation; the insets show the 300-nm-thick and 500-nm-thick films samples under 254 nm UV light illumination. Reproduced with permission. [40] Copyright 2018, Springer Nature. D, Phosphor-converting WLEDs based on single-component Cs₂Ag₀.₆₀Na₀.₄₀InCl₆ phosphors. Reproduced with permission. [22] Copyright 2019, American Chemical Society. E, CIE coordinates of the Cs₂Ag₁₋ₓNaₓInCl₆ and Cs₂Agₓ₋₀.₇Na₀.₃In₁₋ₓBiₓCl₆ samples; the insets show the photographs of obtained samples solution under UV light illumination. Reproduced with permission. [90] Copyright 2019, Wiley-VCH. F, Photographs, and (G) CIE coordinates of the Cs₂Ag₀.₇Na₀.₃InCl₆:Bi-based WLEDs at a current of 90 mA. H, Normalized emission intensity of the WLEDs measured over 1000 hours; the inset shows the testing photograph. Reproduced with permission. [92] Copyright 2020, American Chemical Society.

against heat, UV light, and environment oxygen/moisture, as seen in Shi’s study. [104] By combining with a commercial yellow phosphor, Hosono et al. further fabricated a high-performance WLED, and the CIE coordinates can be linearly tuned from (0.15, 0.09) to (0.44, 0.48) by varying the mixing ratio of Cs₃Cu₂I₅ and commercial yellow phosphors, as shown in Figure 9B. Following this work, Saparov et al. demonstrated a series of mixed-halide Cs₃Cu₂Br₃₋ₓIₓ (0 ≤ x ≤ 5) compounds with near-unity PLQY, and the emission wavelength can be adjusted within a range of 443–456 nm. In addition, the joint experiment-theory characterizations indicate that bromination can enable a relatively higher stability for the products. [105] Adopting the modified hot-injection method, spherical-shaped Cs₃Cu₂I₅ nanocrystals with an average diameter of 20 nm and a high PLQY 67% were first synthesized by Han’s
group,[103] and the high PLQY accompanied with a large Stokes shift supports a high conversion efficiency and a low self-absorption, highlighting their applications in lighting and display. In addition to the Cs$_3$Cu$_2$I$_5$, another ternary copper halides, CsCu$_2$I$_3$, is also interesting and begins to attract intensive attention.[93–96] Different from the zero-dimensional structure for Cs$_3$Cu$_2$I$_5$, the CsCu$_2$I$_3$ material is characterized by a typical one-dimensional ribbon-like crystal structure, featuring edge-shared [Cu$_2$I$_3$]$^+$ ribbons surrounded by Cs$^+$ ions.[93,94] Huang and co-workers reported the synthesis of one-dimensional CsCu$_2$I$_3$ single crystals, which exhibit stable white light emission with a high PLQY of ~15.7%.[108] By temperature-dependent PL and transient absorption measurements, the yellow emission from CsCu$_2$I$_3$ single crystal was attributed to the STEs, and its broadband emission corresponds to the CIE coordinates of (0.345, 0.364) and a CCT of 5035 K, belonging to the warm white light. Besides, the stability of this material is also impressive and obviously better than the conventional lead-halide perovskites. As seen in Figure 9C, after a long-term operation for 750 minutes under continuous laser illumination (325 nm), the emission decay of the CsCu$_2$I$_3$ single crystals is very small and ~95% of the luminous efficiency can be preserved. The above features of CsCu$_2$I$_3$ are of particular interest in lighting applications because a single white
emitter can simplify the device structure and avoid the color instability seen in mixed and multiple emitters. Unfortunately, such single-component white light emitter directly as a down-converter always suffers from a poor color-rendering, as observed in lead-free double perovskites Cs$_2$AgInCl$_6$ above, which limits its application in high-quality indoor lighting. To improve the color rendering and realize the full potential of two ternary copper halides, Shi et al. proposed a new two-component strategy for WLEDs by integrating the yellow-emissive CsCu$_2$I$_3$ with blue-emissive Cs$_3$Cu$_2$I$_5$. Thermodynamic phase stability calculations indicate that both CsCu$_2$I$_3$ and Cs$_3$Cu$_2$I$_5$ are stable with respect to decomposition into binary CuI and CsI, suggesting the possibility of their coexistence. Therefore, a CsCu$_2$I$_3$@Cs$_3$Cu$_2$I$_5$ composite with directly white-light emission was synthesized experimentally by a facile one-step solution method. Moreover, the composites exhibited a cold/warm white-light tuning with the CIE color coordinates ranging from (0.39, 0.43) to (0.25, 0.24) by conveniently controlling the mixing ratio of CsI/CuI precursors, as shown in Figures 9D–F. Since both CsCu$_2$I$_3$ and Cs$_3$Cu$_2$I$_5$ are characterized by the broadband emission features, sufficient to cover a wide spectral range. As a result, the resulting white emission achieves a record CRI of 91.6 for lead-free WLED systems (Figure 9G). Besides, the white-light CsCu$_2$I$_3$@Cs$_3$Cu$_2$I$_5$ composites demonstrated an excellent stability against environment oxygen/moisture, heat and UV light, making practical applications of them a real possibility. In the nanocrystalline systems, Vashishtha et al. also achieved all-copper-based white light emission with the CIE coordinates of (0.290, 0.311) by mixing Cs$_3$Cu$_2$I$_5$ nanoplates and CsCu$_2$I$_3$ nanorods in an appropriate ratio of 1:8. As Cs$_3$Cu$_2$I$_5$ and CsCu$_2$I$_3$ are pure iodide phases, the undesired halide migration or exchange observed in lead-halide perovskites can be avoided, and therefore, a pure white emission with an improved long-term operation stability was obtained. While, an indisputable fact is that the excitation source of the proposed two-component WLEDs can only be an UV chip because of the relatively large optical bandgap of Cs$_3$Cu$_2$I$_5$ and CsCu$_2$I$_3$, and the low excitation efficiency of UV chip should be responsible for the compromised luminous efficiency of the resulting WLEDs.

6 | CONCLUSIONS AND PERSPECTIVES

In summary, we have mainly reviewed the progresses during the last few years in the development of lead-free candidates as down-conversion phosphors for WLEDs. By now, non-toxic Sn-, Bi-, Sb-, and In-based perovskites, double perovskites, and Cu-based halides have been demonstrated to possess desirable characteristics for device fabrication, such as facile processability, broadband emission property, and good white light quality (Table 1). However, there are still some issues to address before we can replace the traditionally established lead-based perovskites with these emerging materials to achieve high-performance WLEDs. First, the luminous efficiency of phosphor-converting WLEDs based on lead-free metal halides is far below the industrial requirements. Because of the strong absorption of lead-free metal halides in the UV and deep-UV region, short-wavelength chips (365 or 310 nm) have to be employed as the common excitation source for phosphor-converting WLEDs. Nonetheless, the UV chips suffer from a much lower output efficiency than the blue chips, inducing a great efficiency loss. Applying more efficient Ga$_{1-x}$In$_x$N blue-violet chips (390-450 nm) could solve this drawback but requires the phosphors to have suitable bandgap and Stokes shift. Unfortunately, almost all lead-free metal halides lack the ideal excitation region. The improvement of the luminous efficiency of WLEDs is the result of the joint progress in phosphor-converting materials, excitation source chips, and device structural design. More specifically, the luminous efficiency is determined by the external quantum efficiency of the semiconductor chips, the PLQY of the phosphor-converting materials, and the light extraction rate of the device. Therefore, future efforts could be directed toward the visible-light-excitible materials with high PLQY and the use of applicable device architectures with high extraction rate and efficient thermal dissipation structure. Second, although some lead-free metal halides with an intrinsic broadband emission show many advantages for use in phosphor-converting WLEDs, such as a large Stokes shift reducing the photon self-absorption, enhanced materials stability, and avoidable color separation, their PLQYs are still too low compared with the lead-based perovskites counterparts. Moreover, there is still a lack of comprehensive understanding on the nonradiative recombination processes and defects in these materials. Besides, these broadband emissive materials lack a full coverage of the visible spectrum, such as efficient green and red emission. A deeper understanding on the emission mechanisms of these materials will help boost their PLQY and purposefully regulate their emission wavelength. In addition to the conventional trial approaches, searching for newly lead-free materials with highly efficient emission might be facilitated by computation supported combinatorial chemistry, in which screening of a large number of possible element combinations with tunable band structures could be realized. Third, the CRI is a well-known color quality metric for WLEDs. It describes how well a light source renders the colors of an object compared to an incandescent light or daylight. However, the majority of phosphor-converting
TABLE 1 Summary of the device performances of the phosphor-converting WLEDs

| Active Layer | PLQY (%) | Pump source | CIE (x, y) | CCT (K) | CRI | Lifetime (h) | Ref. |
|--------------|----------|-------------|-----------|---------|-----|-------------|-----|
| (C₅N₄H₁₂Br)₄SnBr₆ | 95 | UV (365 nm) | (0.35, 0.39) | 4946 | 70 | >7 | [48] |
| (OCTAm)₂SnBr₄ | 95 | UV (365 nm) | (0.33, 0.31) | 6530 | 89 | – | [49] |
| (Cs₄N₂H₁₄Br)₄SnBr₆ₓ | 85 | UV (340 nm) | (0.36, 0.38) | 4600 | 85 | >12 | [50] |
| Cs₂SnCl₆:2.75% Bi | 78.9 | UV (365 nm) | (0.36, 0.37) | 4486 | – | – | [51] |
| Cs₂SnCl₆:0.59%Sb | 50.8 | UV (365 nm) | (0.35, 0.34) | 4888 | – | – | [46] |
| Cs₂InCl₅⋅H₂O:Sb³⁺ | 95.5 | UV (365 nm) | (0.35, 0.35) | 4556 | 86 | – | [75] |
| (Cs₂H₂O₆)₂SbCl₅ | 98 | UV (365 nm) | (0.36, 0.33) | 4282 | 82 | – | [66] |
| Cs₂Ag₀.₅Na₀.₅InCl₆ | 86 | UV (365 nm) | (0.40, 0.45) | 4054 | 82 | >1000 | [40] |
| Cs₂AgIn₃₀₈₃Bi₃₀₇Cl₅₀ | 72.2 | UV (370 nm) | (0.38, 0.44) | 4347 | 87.8 | >1000 | [92] |
| Cs₂CuI₂ | 90 | UV (310 nm) | (0.33, 0.35) | 3347 | 84 | – | [107] |
| Cs₂CuI₂ | 80 | UV (310 nm) | (0.34, 0.34) | 5075 | 90.2 | – | [112] |
| CsCu₂Br₂ and Cs₂CuI₂ | 15.7 | UV (325 nm) | (0.35, 0.36) | 5035 | – | >12.5 | [108] |
| CsCu₂I₃ | 50.4 | UV (365 nm) | (0.27, 0.31) | 10000 | – | >580 | [113] |
| CsCu₂I₃ and Cs₂CuI₂ | 50 | UV (310 nm) | (0.32, 0.33) | 6109 | 91.6 | – | [109] |
| CsCu₂I₃ and Cs₂CuI₂ | 46.4 | UV (365 nm) | (0.32, 0.33) | – | – | >10 | [54] |
| (TEBA)₂SbCl₅ | 98 | UV (365 nm) | (0.36, 0.33) | – | – | – | [66] |
| Mn²⁺-K₂SbCl₆ | 37.2 | UV (365 nm) | (0.35, 0.30) | 5068 | 88 | >12 | [70] |

WLEDs based on lead-free metal halides can hardly exceed 90. For color-critical high-level applications, such as cinematography, art galleries, photography, surgery, and jewellery, an ultra-high CRI above 90 is required. Alternatively, a promising approach is to use two or more broadband emissive components as the down-converters to achieve an ultra-high CRI system. Last but not least, the practical applications of WLEDs require to maintain the luminance of nearly 90% of their initial value after 10,000 hours operation, which cannot be achieved by the state-of-art WLEDs at current stage. This is partially because of the ionic nature of such lead-free materials with low formation energy and soft crystal lattices, which make them vulnerable to UV light, heat, oxygen, and moisture. Further investigations into the degradation mechanism of such materials are needed, and various passivation and encapsulation techniques should continue to be exploited. Moreover, unique device configurations such as remote-type WLEDs could mitigate the degradation of the perovskite phosphors. Looking into the future, we expect that future efforts could be directed to address the above issues to achieve eco-friendly WLEDs with high luminous efficiency, brilliant color-rendering, and long operation lifetime.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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