Lead-Free Halide Perovskites for Light Emission: Recent Advances and Perspectives

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Lead-based halide perovskites have received great attention in light-emitting applications due to their excellent properties, including high photoluminescence quantum yield (PLQY), tunable emission wavelength, and facile solution preparation. In spite of excellent characteristics, the presence of toxic element lead directly obstructs their further commercial development. Hence, exploiting lead-free halide perovskite materials with superior properties is urgent and necessary. In this review, the deep-seated reasons that benefit light emission for halide perovskites, which help to develop lead-free halide perovskites with excellent performance, are first emphasized. Recent advances in lead-free halide perovskite materials (single crystals, thin films, and nanocrystals with different dimensionalities) from synthesis, crystal structures, optical and optoelectronic properties to applications are then systematically summarized. In particular, phosphor-converted LEDs and electroluminescent LEDs using lead-free halide perovskites are fully examined. Ultimately, based on current development of lead-free halide perovskites, the future directions of lead-free halide perovskites in terms of materials and light-emitting devices are discussed.

1. Introduction

Recently, lead halide perovskite materials have attracted increasing attention since the reported power conversion efficiency (PCE) of solar cells based on them soared from an initial value of 3.8% in 2009 to 25.2% in 2020.[1] The high PCE originates from exceptional photovoltaic properties of perovskites, including high absorption of light, small exciton binding energy, balanced electron and hole mobilities, long exciton diffuse length, and low defect density.[2] Xiao et al. studies that the underlying reasons in detail, including the electronic configuration of Pb, high electronic dimensionality, and high perovskite symmetry (O₃) for these outstanding properties.[3] The high PCE motivated the researchers to study LEDs. As expected, lead halide perovskites have also been confirmed to be an excellent light emitter in recent years, which have...
been widely studied in light-emitting devices, owing to high PLQY, narrow peak full width at half maximum (FWHM), tunable spectral range, and facile synthesis.\(^4\) Over a span of five years, an ocean of investigations related to lead halide perovskites have been carried out, including doping, surface passivation, surface coating, and postsynthetic treatment.\(^{14,6,5}\) Moreover, these studies have also made great strides in concomitant with outstanding performance.\(^{14}\)

Currently, organic LEDs (OLEDs) and quantum dot LEDs (QLEDs) have been commercialized in display technology, such as OLED mobile phone from Huawei, OLED television from LG, QLED television from Samsung.\(^{21}\) In addition to displays, OLEDs and QLEDs also show potentials for lighting applications. However, OLEDs and QLEDs present some inherent disadvantages. OLEDs possess lower color purity and narrower color gamut. Additionally, OLEDs are fabricated through vacuum-based thermal evaporation, which is not suitable for cost-effective mass production.\(^{18}\) The quantum dots used in QLEDs provide better color purity, excellent stability, and high efficiency, but they (especially the core-multiple–shell structures) require extremely complex high-temperature synthesis and expensive raw materials.\(^9\) The comparisons of perovskites, quantum dots, and organic fluorophores for photoluminescence (PL), FWHM, PLQY and color gamut are listed in Table 1.

In addition to the superior optical properties, the synthesis process of perovskites is quite simple at room or relatively low temperature (<180 °C).\(^{10}\) More importantly, perovskites possess balanced carrier mobility and long exciton diffusion length, which are beneficial to LEDs.\(^{11}\) Owing to the above excellent properties, lead halide perovskite light-emitting devices have obtained superior external quantum efficiencies (EQEs) exceeding 20% in recent years.\(^{12}\)

Lead halide perovskites have superior properties for light emission, however, the existence of lead element restricts their mass applications. It is noteworthy that one of the degradation products of lead halide perovskites embraces water-soluble Pb salt.\(^{13}\) A great deal of medical research has reported the severe toxicity of lead. Low-level lead exposures can disturb the neurological, cardiovascular, and hematopoietic systems.\(^{14}\) The Centers for Disease Control and Prevention (CDC) of the United States recommends <10 μg per deciliter blood levels to be safe.\(^{15}\) In 2003, the European Union released “Directive on the restriction of the use of certain hazardous substances containing lead in electrical and electronic equipment,” which demanded lead-free in electrical and electronic equipment. Thus, developing environmentally benign lead-free halide perovskites and perovskite analogue materials with excellent optical and optoelectronic properties is urgent and essential.

Since CH\(_3\)NH\(_3\)SnI\(_3\) was first introduced by Snaith’s team to serve as a photoactive material, a multitude of lead-free halide perovskite materials have been reported, which are widely applied in solar cells, photodetectors, LEDs, and field-effect transistors (FETs).\(^{16}\) Figure 1 lists the possible replacement of lead in perovskites and perovskite analogues. In fact, some lead-free perovskites should be known as perovskite analogues from the strict definition of perovskites that are confined in 3D connected BX\(_6\) octahedra (the crystal cells). Herein, we term the perovskite analogues as perovskites for convenience, aligned with the common definition.

In this review, we introduce the deep-seated reasons for halide perovskites with excellent optical properties, and discuss the relatively inferior luminescent performances of lead-free halide perovskites, which can give some foundations for the development of the lead-free halide perovskites. In addition, the design and synthesis methods of lead-free halide perovskites are systematically summarized. Subsequently, a comprehensive review on optoelectronic characteristics of lead-free halide perovskites with different molecular dimensionalities is provided, including single crystals, nanocrystals, and thin films. Their light-emitting applications are also fully delved. Finally, we put forward some insightful considerations toward future development of lead-free perovskites and their LEDs.

2. Excellent Properties of Lead Halide Perovskites for Light Emission

In order to understand lead-free halide perovskites, it is essential to know their exceptional properties for light emission. The defect tolerance, bandgap type, and exciton binding energy are several key factors.

2.1. Defect Tolerance

Defect tolerance exists in lead halide perovskite thin films and nanocrystals.\(^{19}\) Taking nanoscale materials as an example, defects cannot be ignored due to a high surface to volume ratio.\(^{20}\) In most cases, defects serve as an adverse role and need to be eliminated to the maximum extent. In order to illustrate the importance of defect tolerance, we compare the defect-intolerant conventional semiconductor with defect-tolerant lead halide perovskites.\(^{21}\)

Figure 2a demonstrates the electronic structure differences between conventional semiconductors (CdS, InP) and lead halide perovskites. For conventional semiconductors, electronic surface passivation is necessary to improve PLQY such as CdSe/ZnS core/shell nanocrystals, wherein ZnS shell passivates CdSe surface to obtain approximately unity PLQY, while lead halide perovskites do not require any surface passivation to get bright photoluminescence.\(^{26}\) The former is called defect intolerance, and the latter is defect tolerance.\(^{27}\) In other words, defect tolerance means that even if there are many structural defects in the materials, these defects will not lead to electronic traps, namely having a clean bandgap. Early in 2014, Zakutayev et al. pointed...
out that the valence band of semiconductors composed by antibonding states could form shallow defect levels, which did not have an effect on their properties. Moreover, Pandey et al. demonstrated that different orbital characteristics between valence band (VB) and conduction band (CB) might introduce the shallow trap states. In perovskite systems, VB has antibonding nature, whereas CB consists of spin–orbit coupling. Taking CsPbI$_3$ as an example, the VB is attributed to Pb(6s)–I(5p) antibonding interaction and CB originates from Pb(6p) spin–orbit effect. That may explain the defect tolerance of bulk halide perovskites. For lead halide perovskite nanocrystals, the dangling bonds and surface organic ligands need to be considered, which have possibilities to form trap states. Dangling bonds are nonbonding in nature and arise between bonding and antibonding states, and bonding orbitals cannot lead to the formation of VB and CB, which suggests that a deep state in bandgap will not be formed. Besides, some calculated results reveal that point defects in CsPbBr$_3$ only form shallow states, and the defect-tolerance characteristic of CsPbBr$_3$ nanocrystals is attributed to lacking of bonding–antibonding interaction between the CB and VB. As for surface organic ligands, Infante’s group combined theory models and experiments to validate that the electronic structure of perovskite nanocrystals changed slightly after removal of ligands from surface as shown in Figure 2b. In addition, Yan’s group reported the calculated transition energy levels of point defects in MAPbI$_3$ (including interstitials or antisites) had higher formation energy and gave rise to excellent defect tolerance of perovskite nanocrystals as shown in Figure 2c. Under different conditions (halide-poor or halide-rich), the formation energy of defects varies. In short, these researches suggest that defect tolerance is a pivotal factor for lead halide perovskite nanocrystals with high PLQY.

2.2. Bandgap Type

It is worthy of highlighting that bandgap type is also a crucial factor in influencing the optical characteristic of materials. Tailoring bandgap magnitude has been studied with a great deal...
work. More importantly, the type of bandgap (direct or indirect) is also a significant characteristic either for photovoltaics or light emission. It must be mentioned that the relative crystal momenta of the conduction band minimum and valence band maximum decides whether a bandgap is direct or indirect. As shown in Figure 2d, there is an apparent difference in direct bandgap and indirect bandgap. For direct bandgap materials, the process of absorption and recombination are only invoked by photons, which can lead to high PLQY. In comparison, there is a process involving assistant phonons in indirect bandgap materials, which can form the thermal energy to decrease PLQY during the transition process. In lead halide perovskites, direct bandgap characteristic is vital to obtain near-unity PLQY.

2.3. Exciton Binding Energy (E_b)

Apart from defect tolerance and bandgap type, exciton binding energy is also an important factor to impact the optical characteristics of materials. An exciton refers to a pair of excited electron and hole, which exist mutual attraction via a Coulombic interaction to form a neutral quasiparticle. Exciton binding energy means that the binding ability of exciton. Excitons can be classified as Frenkel excitons and Wannier excitons according to the relationship between lattice constant (a) and Bohr radius (r_B) as shown Figure 2c. Generally, Frenkel excitons have a small Bohr radius of 5 Å with a large exciton binding energy ranging from 500 to 1000 meV, whereas Wannier excitons have a large Bohr radius in concomitant with a small exciton binding energy of 10–30 meV. At room temperature, the exciton with a binding energy smaller than thermal energy kT (26 meV) tends to dislocate into free carriers. Free carriers are opposed to localized excitons and can freely diffuse through the host lattices to propagate the excitation energy without transporting net electric charge. Thus, materials with smaller exciton binding energy are more suitable for solar cells. However, based on totally different design rules, a larger exciton binding energy is required for light emission, which promotes the radiative recombination of excitons efficiently. A series of research demonstrated that exciton binding energy is higher in confined structures, such as nanocrystals (<100 nm in at least one dimension), including nanoplates, nanowires, nanorods and quantum dots. The confined structures based on dimensionally physical barriers suppress the exciton dissociation and enhance radiative recombination to improve PLQY of materials.

Zheng et al. reported the exciton binding energy of MAPbBr_3 nanocrystals (E_b = 0.32 eV) was 3.8 times higher than that of the corresponding bulk crystals (E_b = 0.084 eV). The higher E_b contributed to enhanced PLQY (<0.1% for bulk crystals). Simultaneously, structurally formed potential barriers embedded in the crystal lattice, namely, low-dimension perovskites also
have confinement effect.\(^{42}\) Besides, it is worth noting that low-dimension perovskites (see below) at the molecular level possess larger exciton binding energies, whose amplification is attributed to not only the quantum confinement effect but also the dielectric enhancement.\(^{43}\) The organic layers with low dielectric constant have poor screening effect on the attraction between electrons and holes in the inorganic layers, which can improve the exciton binding energy as experimentally validated.\(^{44}\)

Early research reported that exciton binding energy can be improved up to four times when exciton is confined in two dimensions.\(^{45}\) Quantum well structure in 2D perovskites confines electrons and holes within the well, leading an improvement of larger exciton binding energies and radiative recombination due to the very different dielectric constants of the “well” and “barrier” as shown in Figure 2f.\(^{11}\) Ishihara showed a huge change of exciton binding energy which ranged from 1.633 eV for 3D perovskites to 3.42 eV for 0D perovskites and demonstrated the effect of smaller dielectric constant of barrier layers.\(^{46}\) Additionally, some research manifested that the halide and the thickness of the inorganic layers had some influences on exciton binding energy and bandgap.\(^{47}\) One research reported \(E_b = 220 \text{ meV}\) and \(E_b = 2.58 \text{ eV}\) for PEA\(_2\)PbI\(_4\) in comparison with \(E_b = 356 \text{ meV}\) and \(E_b = 3.40 \text{ eV}\) for PEA\(_2\)PbBr\(_4\) (PEA = C\(_6\)H\(_{12}\)CH\(_2\)CH\(_2\)NH\(_2\)).\(^{48}\) Nurmiikko’s group reported that PEA\(_2\)(MA)\(_2\)PbI\(_3\) family had different bandgap and exciton binding energy with different thickness of inorganic layers.\(^{49}\) In summary, a larger exciton binding energy based on confined structures is considered to be beneficial to light emission. However, every coin has two sides. Auger recombination increases with the increase of exciton binding energy. Compared with 3D perovskites, the rate of Auger recombination is improved in 2D perovskites.\(^{49}\) In order to illustrate the corresponding effects, Table 2 summarizes the characteristics of defect tolerance, bandgap type and exciton binding energy of some halide perovskites.

In addition to the above discussion, there is one exceptional case that deserves more attention. Cs\(_2\)AgInCl\(_6\) with direct bandgap displays an extremely low PLQY, whereas the PLQY of Cs\(_2\)Ag\(_{0.6}\)Na\(_{0.4}\)InCl\(_6\):0.04Bi\(^{3+}\) reaches 86% after introducing Na\(^+\) and Bi\(^{3+}\) ions. The underlying mechanism bringing difference is worth considering developing excellent lead-free halide perovskite materials with superior performance. There are two main reasons for the low PLQY of halide double perovskites Cs\(_2\)AgInCl\(_6\). On the one hand, the emission of halide double perovskites Cs\(_2\)AgInCl\(_6\) belongs to parity-forbidden transitions. On the other hand, the wave function distributions of electron and hole exist small overlaps. After alloying with Na\(^+\), the parity-forbidden transition was removed by breaking the inversion symmetry via substituting partial Ag\(^+\) ions. In addition, theoretical calculation revealed that Na\(^+\) alloying improved the wave function overlaps between electron and hole. After doping a small amount of Bi\(^{3+}\), the PLQY of Cs\(_2\)Ag\(_{0.6}\)Na\(_{0.4}\)InCl\(_6\):0.04Bi\(^{3+}\) was further improved to 86% via passivation of defects.\(^{60}\)

In conclusion, lead-free halide perovskites with defect-tolerance, direct-bandgap, and larger exciton binding energy are beneficial for light emission. More importantly, some significant strategies to adjust bandgap type, passivate defects, increase exciton binding energy, break parity-forbidden transition, and seek for defect-tolerant lead-free halide perovskites are in demand. Moreover, some methods have been proved to be effective and feasible, such as doping, post-synthetic treatment, and developing low-dimension perovskites or perovskite nanocrystals.\(^{51,24,36,61}\)

### Table 2. Defect tolerance, bandgap type, and exciton binding energy (\(E_b\)) of some halide perovskites (NCs, nanocrystals; SCs, single crystals; BCs, bulk crystals).

| Material         | Defect tolerance | Bandgap type | \(E_b\) [meV] | PLQY [%] |
|------------------|------------------|--------------|---------------|---------|
| CsPbCl\(_2\) NCs | Yes              | Direct       | 67\([50]\) 75\([40]\) | 96.5\([51]\) 97\([48]\) 88\([60]\) |
| CsPbBr\(_2\) NCs | Yes              | Direct       | 47\([50]\) 40\([32]\) | 96\([49]\) 97\([31]\) 100\([31]\) |
| CsPbi\(_3\) NCs  | Yes              | Direct       | 25\([50]\) 20\([40]\) | 95\([46]\) 96\([40]\) 100\([23]\) |
| (OCTAm)\(_2\)SnX\(_4\) | –               | Direct       | –             | 95 \pm 5\([32]\) |
| Cs\(_2\)Bi\(_2\) Br\(_2\) NCs | Yes\([17]\) | –           | 210.7         | 19.4\([38]\) |
| MA\(_2\)Bi\(_2\)Br\(_4\)Cl NCs | Yes\([17]\) | –           | 259.1         | 54.1\([59]\) |
| Cs\(_2\)AgIn\(_3\) Bi\(_2\)Cl\(_6\) NCs | –              | Direct       | 496           | 36.6\([24]\) |
| Cs\(_2\)AgInCl\(_6\) BCs | –              | Direct       | 250           | <0.1\([40]\) |
| Cs\(_2\)Ag\(_{0.6}\)Na\(_{0.4}\)InCl\(_6\):0.04Bi\(^{3+}\) BCs | –              | –           | –             | 86 \pm 5\([60]\) |
| Cs\(_2\)Cu\(_2\)I\(_5\) SCs | –              | Direct       | 490           | 91.2\([61]\) |
| Cs\(_2\)AgBiCl\(_6\) NCs | –              | Indirect     | –             | 6.7\([62]\) |
| Cs\(_2\)AgBiBr\(_6\) NCs | –              | Indirect     | –             | 0.7\([62]\) |
| Cs\(_2\)AgBi\(_2\)I\(_6\) NCs | –              | Indirect     | –             | <0.1\([62]\) |

3. Design and Synthesis of Lead-Free Halide Perovskites

3.1. Design of Lead-Free Halide Perovskites

Perovskite materials have a general chemical formula of ABX\(_3\), where A usually refers to Cs\(^+\), Rb\(^+\), CH\(_3\)NH\(_2\) (MA\(^+\)) or CH(NH\(_2\))\(_2\)\(^+\) (FA\(^+\)), B is a divalent lead cation (Pb\(^{2+}\)), and X stands for halogen (Cl\(^-\), Br\(^-\), I\(^-\)). The common way of searching for lead-free halide perovskites is substituting Pb\(^{2+}\) by group 14 metal elements (Sn and Ge), group 15 metal elements (Sb and Bi) and other metal elements. Notably, Goldschmidt tolerance factor (\(t\)) and octahedral factor (\(\mu\)) are two important parameters to indi-
Figure 3. Halide perovskite structures with different dimensionalities at the molecular level. a) The unit cell of 3D perovskite. b) The <010> orientation projection of 3D halide perovskites. c) The crystal structure of <001>-oriented 2D perovskite (n = 1). d) The crystal structure of <001>-oriented quasi-2D perovskite (n = 2). e) The crystal structure of <110>-oriented 2D perovskite (n = 2). f) The crystal structure of <111>-oriented 2D perovskite (n = 2). g) The crystal structure of 1D perovskite with octahedra connecting in a chain form. h) The crystal structure of 0D perovskites with the isolated octahedra.

The octahedral factor $\mu$ can be used to estimate the stability of octahedra. Generally speaking, perovskite structure is stable when the octahedral factor $\mu$ ranges from 0.442 to 0.895. $\mu = \frac{r_B}{r_X}$, where $r_A$, $r_B$, and $r_X$ are the ionic radii of A, B, and X, respectively. To a large extent, larger A cations cannot form 3D crystal structures; they lead to warp, damage, or transform of structure to form lower-dimensional crystals. In addition, the B cations are also considerable to keep charge neutrality. There are isovalent replacement ($\text{Sn}^{2+}$, $\text{Ge}^{2+}$, $\text{Cu}^{2+}$, $\text{Y}^{2+}$, etc.) and heterovalent replacement ($\text{Ag}^{+}$, $\text{Cu}^{+}$, $\text{Bi}^{3+}$, $\text{Sn}^{4+}$, $\text{Ge}^{4+}$, $\text{Pd}^{4+}$, etc.). All possible replacements of lead element are presented in Figure 1.

The formulas of lead-free halide perovskite vary as a result of the different replacements, which are $\text{AB(II)X}_3$, $\text{A}_2\text{B(IV)X}_6$, $\text{A}_3\text{B(III)X}_9$, $\text{A}_4\text{B(III)B(V)X}_{12}$, $\text{A}_4\text{B(II)B(III)X}_{12}$ and other perovskite derivatives. Double, triple, quadruple, and defect/vacancy perovskites have their general formulas of $\text{A}_2\text{B(II)B(III)X}_{6}$, $\text{A}_3\text{B(III)X}_9$, $\text{A}_4\text{B(III)B(V)X}_{12}$, $\text{A}_4\text{B(II)B(III)X}_{12}$ and $\text{A}_2\text{B(IV)X}_6$, respectively. These different types diversify the halide perovskites. Notably, the effects of mixed charges in the B sites are multiple. First, it can change the bandgap magnitudes and bandgap types. Second, it can change the optical characteristics, such as nonemission to emission, the emission color, and the emission range. Third, it can also improve the stability of perovskites.
Halide perovskites can be categorized as 3D, 2D, 1D, and 0D at the molecular level according to different arrangements of metal halide octahedra [BX₄]ⁿ⁺ as shown in Figure 3. When smaller size cations are in A site (such as Cs⁺, MA⁺ and FA⁺), metal halide octahedra [BX₄]ⁿ⁻ can form corner-sharing 3D networks (Figure 3b). When A is replaced by larger size organic cations, 2D structures are formed where [BX₄]ⁿ⁻ octahedra connect in layered or corrugated sheets that are sandwiched between large organic cations. 2D and corrugated 2D organometallic halide perovskites are formed by splitting along lattice orientations <001> and <110> from 3D perovskites, which are identified as Ruddlesden–Popper perovskites. 2D Ruddlesden-Popper halide perovskites can be expressed as (A')ₙ(A)ₙ₋₁BX₄₋ₙ[X₃₋ₙ]⁺, where A stands for small size cations, such as Cs⁺, MA⁺, and FA⁺. A’ represents large organic cations between inorganic sheets (usually with long alkyl chains or a benzene ring), B refers to bivalent metal cations (Sn²⁺ and Pb²⁺), X refers to halides, and n stands for the number of metal halide monolayer between the insulating organic layers. n = 1 represents single layer inorganic octahedra (strict 2D perovskites, Figure 3c), n = 2–5 stands for quasi-2D perovskites (Figure 3d), and n = ∞ refers to 3D perovskites.[68] Notably, corrugated 2D perovskites can be formed along the <110> orientation to cut the 3D perovskites, as depicted in Figure 3e.[69] There are also <111> oriented 2D perovskites as shown in Figure 3f. For 1D perovskites, [BX₄]ⁿ⁻ octahedra are connected in a chain form (corner-sharing, edge-sharing, or face-sharing), and the chemical formulas rely on the connecting ways of octahedra BX₄ and the organic cations (Figure 3g).[70]

In 0D halide perovskites, individual metal halide octahedra are completely surrounded by organic cations and isolated from each other. The general formula is expressed as A[BX₄]n, where A refers to monovalent organic cations and [BX₄]ⁿ⁻ refers to isolated octahedra (Figure 3h). It is worth noting that the above-mentioned categories are based on molecular level rather than morphological 2D nanosheets/nanoplatelets, 1D nanowires/nanorods, and 0D quantum dots. For example, morphological 0D perovskites are called as quantum dots, in which the [BX₄]ⁿ⁻ octahedral units are connected with strong interactions via corner-sharing to form a 3D framework.[42] Owing to the different connectivity of the [BX₄]ⁿ⁻ octahedral units, the 0D perovskites at the molecular level display extremely different optoelectronic characteristics in comparison with the morphological 0D quantum dots. However, there are also some relationships between molecular levels and morphological levels. On the one hand, 1D and 0D organometal halide perovskites at the molecular level can be regarded as bulk assemblies of 1D quantum wires and 0D molecules/clusters, respectively. The completely isolated octahedra in these low-dimensional 1D and 0D perovskites enable the materials to exhibit the intrinsic properties of the individual octahedron. On the other hand, the low dimensionality both at the molecular level and morphological level possess quantum confinement effect.[42,70] The low dimensionalities (2D, 1D, 0D) of perovskites that will be talked below refer to the molecular level.

Currently, bulk crystals, thin films, and colloidal nanocrystals of halide perovskites are all considered as potential materials for various optoelectronic applications.[10,25,71] Based on this background, we systematically summarize their synthesis methods.

### 3.2. Synthesis of Lead-Free Halide Perovskite Single Crystals

#### 3.2.1. Synthesis of Lead-Free Halide Perovskite Single Crystals

Single crystal can be used to analyze basic structure and physical properties of materials. It also has a low trap density and is favorable for the radiative recombination.[72] Early in 1978, halide perovskite single crystals were synthesized by Weber.[73] Afterwards, there was a great number of single crystal growth methods of halide perovskite reported, including temperature-lowering crystallization (TLC), traditional solvolothermal method, inverse temperature crystallization (ITC), antisolvent vapor-assisted crystallization (AVC), and slow evaporation method (SEM).[74] These methods are to obtain supersaturated precursor solution, adjust the solubility, and induce crystallization. Herein, we summarize the representative lead-free halide perovskite single crystal growth methods.

Temperature-lowering crystallization (TLC) is performed by accurately lowering the temperature of preferred seed solution to induce the oversaturation of the solute. Subsequently, the saturated aqueous perovskite precursor HX (X = Cl, Br, I) solution, which contains inorganic metal ions and organic halide ions, grows halide perovskite crystals slowly. 2D Sn₃-based single crystals (Cs₄H₄NH3)₂(CH₃NH₃)SnBr₃ and (CH₃NH₃)₃SnBr₃ single crystals with dimensions of 20 × 16 × 10 mm³ and 8 × 6 × 5 mm³ by the same method. Taking CH₃NH₃SnI₃ for example, a certain amount of SnO and CH₃NH₂I were dissolved in a mixture of H₂I and H₂PO₃ to form a clear solution. Notably, H₂PO₃ acted as a reducing agent to stabilize Sn²⁺ and I⁻ ions.[72] 0D (Cs₄H₄NH₃)₂Bi₂O₅Sb₂O₅Br·H₂O single crystals were also grown similarly.[72] Rb₂Bi₃Cl₁₀ single crystals were synthesized by a traditional hydrothermal method with a temperature-lowering process. The freezing rate of 2 °C h⁻¹ was crucial to the growth of these single crystals.[79] The temperature-lowering method is a simple and stable process to grow high-quality big size single crystals. However, this method is not appropriate for materials with low solubility at high temperatures. In this condition, inverse temperature crystallization (ITC) method is suitable. Song’s group reported that Cs₃Sb₂Br₉ single crystals were grown by ITC method, where CsBr and SbBr₃ with certain proportions were dissolved in DMSO at room temperature. Then, the solution was filtered with 0.2 mm pore size. In the end, the filtrates were placed in a vial and was kept in a 90 °C oil bath for 3 h to obtain the final product.[80] It should be noted that ITC method may generate more defects, because the grow rate of single crystal is difficult to control.

Antisolvent vapor-assisted crystallization (AVC) is appropriate for materials with high solubility in some solvents but poor solubility in other solvents. Herein, an appropriate antisolvent
chosen to diffuse slowly into a solution containing the precursors, which can lead to the crystallization of halide perovskites. Abulikemu et al. grew (CH$_3$NH$_3$)$_3$Bi$_2$I$_9$ single crystals by AVC. First, CH$_3$NH$_3$I and BiI$_3$ with certain ratios were dissolved in γ-butyrolactone, and the above reaction vessel was placed in an antisolvent (anhydrous dichloromethane) without any direct contact. Then, antisolvent diffused to the CH$_3$NH$_3$BiI$_3$ solution after one day, which changed the solubility and thus promoted the growth of single crystals.[81] Cs$_3$Cu$_2$I$_5$ single crystals were also synthesized similarly. As shown in Figure 4b, filtered Cs$_3$Cu$_2$I$_5$ solution was injected in a vial and wrapped with a paraffin membrane with a small hole. The vial was put in a beaker where there was methyl alcohol (MeOH) as an antisolvent. Moreover, this beaker was sealed. Notably, the paraffin membrane has two effects which not only balanced the antisolvent atmosphere but also suppressed its evaporation. Subsequently, Cs$_3$Cu$_2$I$_5$ single crystals were obtained after the breaker was put on hotplate at 60 °C for 48 h.[61] (Ph$_4$P)$_2$SbCl$_5$ (Ph$_4$P = tetraphenylphosphonium) single crystals were also synthesized similarly and demonstrated excellent optical properties.[82] Generally, the crystal grow rate of AVC is relatively slow, but the quality of the obtained single crystals is decent.

Slow evaporation is also a facile and traditional method for single crystal growth. Growth of (CH$_3$NH$_3$)$_3$Bi$_2$I$_9$ single crystals were reported, where the methanol solution containing CH$_3$NH$_3$I and BiI$_3$ was ultrasonicated for ≈0.5 h, then transferred to a clean vial and evaporated slowly overnight at room temperature.[83]

Notably, large bulk single crystals may be more convenient when analyzing the intrinsic characteristics of materials. However, large area and thin single crystals are in demand in terms of optoelectrical device applications in favor of carrier transport. Researchers are making great efforts to optimize the crystallization process toward simple and green processes and to control the nucleation in order to obtain proper single crystals to meet the different application requirements. Intriguingly, different facets of one single crystal demonstrate different characteristics, namely, the anisotropy phenomenon. Hence, facets engineering can be considered to exploit high-performance single crystals.

3.2.2. Synthesis of Lead-Free Halide Perovskite Colloids

Hot injection and recrystallization are widely applied to colloidal nanocrystal synthesis either for lead-based or lead-free halide perovskites.[33b,84] Figure 4c shows the synthesis of Cs$_3$Sb$_2$I$_9$ via hot injection. SbI$_5$ was dissolved in a mixture of surfactants and solvent mostly with oleic acid (OA), oleylamine (OLA) and 1-octadecene (ODE). Afterwards, the preheated Cs-oleate precursor was injected in the aforementioned solution at a specific temperature; after reacted for a while, the synthesis was quenched using an ice bath. It is noteworthy that the size and morphology can be tailored by the injection temperature, reaction time, and precursor concentration. During the process of synthesizing Cs$_3$Sb$_2$I$_9$ nanocrystals, a different reaction temperature leads to a different morphology. Subsequently, a lot of lead-free halide perovskites were synthesized through hot injection method.[84b,85] Locardi et al. utilized diphenyl ether and benzoyl chloride to prepare Cs$_5$AgInCl$_4$ and Mn$^{2+}$ doped Cs$_5$AgInCl$_4$ double perovskite nanocrystals.[86] Zhang et al. synthesized (OAm)$_2$SnBr$_4$ (OAm = C$_{18}$H$_{35}$NH$_3$) belonged to 2D structural dimensionality.[86] The materials were obtained by injecting a SnBr$_2$-TOP solution into
a solution containing ODE, OA and OLA at 180 °C under a N2 atmosphere. The reaction was maintained for 10 s and was quenched by ice water swiftly. Subsequently, the product was obtained by adding hexane and centrifuging. The XRD measurement revealed the presence of a periodic 2D structure of the (OAm)2SnBr4 perovskite with a regular interval of 2.3°.

Generally, perovskite nanocrystals synthesized via hot injection method possess uniform size and shape. However, there are also some disadvantages, including strict synthesis temperature, not suitable for mass production, and inert gas atmosphere protection. Apart from hot injection method, recrystallization (RP), including ligand-assisted recrystallization (LARP) and antisolvent recrystallization (ASRP), is also of great interest due to their facile and high-yield fabrication. In 2016, Zeng’s group reported that CsPbX₃ (X = Cl, Br, I, or a mixture of them) perovskite nanocrystals were synthesized by modified LARP. Zhang et al. first examined the solubility of CsBr and SbBr₃ in typical solvents. Then they found that the most suitable solvents were N,N-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), and the antisolvent was octane (Figure 4d). During the synthesis process, OA and OLA served as surface ligands to control the morphology and crystallization.[90] In most RP synthesis process, DMSO and DMF often serve as universal solvents while the choices of antisolvent are diverse, such as toluene, iso-propanol, ethanol, and octane.[24,59] Han’s group reported a series of lead-free halide double perovskite nanocrystals synthesized via RP, where iso-propanol was chosen as an antisolvent. Typically, to synthesize Cs₂Ag₁₋ₓAₓBiBr₆, CsCl, AgCl, InCl₃, and BiCl₃, with a certain proportion were dissolved in DMSO to form a precursor solution. Then this precursor solution was injected into iso-propanol under vigorous stirring. Finally, the product was obtained by centrifugation. If some OA was previously added in iso-propanol, then OA-capped halide double perovskite nanocrystals were obtained. Experiments showed that OA-capped halide double perovskite nanocrystals displayed superior emission properties than OA-free nanocrystals. That was attributed to the passivation effect of OA and that promoted the radiative recombination.[24]

There are other ways to synthesize lead halide perovskite colloids. However, for the lead-free halide perovskite colloidal system, only the above two methods have been reported. We believe other methods and new techniques will be used for the synthesis of lead-free halide perovskite colloids.

3.2.3. Synthesis of Lead-Free Halide Perovskite Thin Films

Spin-coating and vapor deposition are two common approaches. To obtain the films fabricated by spin-coating method, metal halide salts (such as SnBr₃, BiBr₃) and organic or inorganic halide salts (such as MBr, CaBr, CsI) were dissolved in an organic solvent (DMF, DMSO, GBL (γ-butyrolactone), NMP (N-methylpyrrolidone), ACN (acetonitrile) or a mixture of them) to form a precursor solution, and then it was spin-coated on substrates along with thermal annealing process. It is worth exploring the processing time and temperature for different precursor composition to get high-quality thin films.

Cs₂AgBr₃ thin films were reported for the first time by Bein’ group in 2017. CsBr, AgBr, and BiBr₃ were dissolved in DMSO to form a precursor solution at 75 °C, and the substrate was also kept at 75 °C. Then precursor solution was spin-coated on the substrate at 2000 rpm for 30 s, subsequently annealed at 285 °C for 5 min to get double perovskite phase thin films.[88] To get higher-quality Cs₂AgBiBr₆, thin films, Ning et al. reported that Cs₂AgBiBr₆ single crystals were dissolved in DMSO under a temperature range from 100 to 130 °C. After a complete dissolution, the solution was spin-coated onto the substrate at 3000 rpm for 40 s at room temperature. The obtained thin films were annealed at 250 °C for 5 min to crystallize further.[89] The thickness of the film was adjusted by varying the concentration of the precursors.[90] The annealing temperature is also vital for the thin film’s quality. Sun’s group fabricated CsSnI₃ thin films under different annealing temperatures. Increasing the annealing temperature made a coarse grain size.[91]

Antisolvent washing is also considered to be an important procedure to fabricate perovskite thin films in the solution process.[92] Yu et al. reported that Cs₂Bi₁₋ₓIxₙBrₙ₊₁ perovskite thin films were fabricated by further antisolvent washing. Chlorobenzene was utilized as the antisolvent in this process. The thin films were fabricated via depositing the precursor, then chlorobenzene was drop-cast on them and the films were annealed at 200 °C for 10 min. There was a huge difference with and without chlorobenzene treatment. The surface morphologies consist of grains, and the thin films became more compact and dense after chlorobenzene treatment.[93] In the antisolvent method, the solubility of the precursors in solvent and antisolvent has a substantial influence on the crystallization process composed of nucleation and growth process. Therefore, the choice of solvent and anti-solvent is pivotal.[94]

As shown in Figure 4e, a simple spin-coating method was applied to prepare the ultrathin nanosheets of AₓBi₁₋ₓIₙ. Briefly, a precursor solution containing CsI (or MAI) and BiI₃ was deposited on a glass substrate via spin-coating and heating to obtain AₓBi₁₋ₓIₙ thin films. In order to improve the quality, a dissolution-recrystallization process was applied, which make the thin films good crystallinity compared with the simple spin-coating only. A small amount of polar organic solvents, CH₃OH and DMF were then spin-coated onto the AₓBi₁₋ₓIₙ thin films to assist recrystallization. Finally, the sample was annealed to remove the solvent, and the ultrathin films were thus formed.[95]

Two-step deposition also plays an important role in improving thin film’s morphology. Panthani’s group reported that AₓBi₁₋ₓIₙ (A= FA⁺, MA⁺, Cs⁺ or Rb⁺) thin films were fabricated with it. First, a certain amount of BiI₃ dissolved in a mixture of tetrahydrofuran (THF) and DMSO was deposited onto the substrate, and spin coated at a certain temperature for some time in
concomitant with annealing. Then Al solution was spin coated onto the BiI₃ thin films and followed by annealing. In comparison with one-step deposition, A/B₁I₃ thin films synthesized by two-step deposition are smoother and more homogeneous in grain size. \[98\]

Vapor-based deposition technique is another common approach in fabricating halide perovskite thin films. \[99\] As shown in Figure 4f, Cs₂TIBr₃ thin films were synthesized via vapor deposition. \[97\] The CsBr thin films predeposited onto the substrate were annealed in a TIBr₄ vapor atmosphere at 200 °C. In this process, annealing temperature and annealing time were deterministic. Chen et al. fabricated highly stable and efficient CsSn₀.₅Ge₀.₅I₃ thin films by single-source evaporation method. \[100\] Wu’s group fabricated CsSnBr₃ thin films via vacuum vapor deposition, which endowed the thin films with a grain size of 60 nm. \[101\] Wang et al. presented a sequential vapor deposition procedure to fabricate double perovskite Cs₂AgBiBr₆ thin films with large grain sizes and uniform and smooth surface. \[102\]

Spin-coating and vapor deposition techniques have their own advantages and disadvantages. Spin-coating method is a low-cost synthesis but not suitable for mass production. Vapor-based deposition method presents apparent advantages for large area preparation and controllability.

In addition to the spin-coating and vapor deposition techniques, some particular fabrication methods were also developed to fabricate thin films. Gao’s team utilized a different ultralow vacuum deposition route to fabricate highly compact, pinhole-free and large-grained MA₁Bi₁I₃ thin films, which is a gas-solid reaction circumventing any solvent contact. \[103\] Yokoyama et al. also developed a controlled gas-solid reaction to fabricate perovskite single crystals. \[104\] Yang’s group reported Sn-based high-quality perovskite thin films with large-area via a green solution process. A gas pump is applied during the fabricating thin films by lowering the pressure so to remove the solvent quickly. \[105\] In addition, PHABI₃⁻ (PHA = C₆H₅NH₃⁺) thin films were synthesized by the above method when the pressure was lowered from 1500 to 30 000 Pa, which displayed superior humidity stability up to 330.d. \[106\]

It is worth highlighting that perovskite single-crystal thin films raise wide attention in various optoelectronic applications. \[107\] They possess the characteristics of both single crystals and polycrystalline thin films. Compared with polycrystalline thin-films and nanocrystals, perovskite single crystals have lower defect densities, higher carrier mobility and longer diffusion lengths owing to the absence of grain boundary. However, inefficient carrier transport and accumulation behavior will take place due to the difference between short carrier diffusion length and perovskite single crystal thickness. In order to solve the above problems, perovskite single-crystal thin films with proper thickness (e.g., < 200 μm) are getting more attention. So far, lead-free halide perovskite single-crystal thin films have not been reported.

4. Structural and Optical Properties of Lead-Free Halide Perovskite Materials

Some reported researches manifest that the photophysical properties are exceedingly various for halide perovskites with different dimensionalities. We here summarize common photophysical processes and characteristics of halide perovskites with different dimensionalities at the molecular level. 3D, quasi-2D, and 2D halide perovskites for light generation generally demonstrate small Stokes shifts, narrow FWHM, and lifetime on the order of nanoseconds. These stem from the direct excited-state transitions, namely the recombination of free excitons. The process is that electrons transit from the ground state to the excited state, generating holes in the ground state under the light excitation. Then electrons and holes recombine radiatively for light emission, as shown in Figure 5a. \[70\] Especially for quasi-2D halide perovskites, there is more than one phase. The multiphase causes channel energy transfer across an inhomogeneous energy landscape, concentrating carriers on smaller bandgap emission (Figure 5b). \[107\]

Unlike typical narrow emission of 3D and 2D, corrugated 2D and 1D perovskites show broad-band emissions with large Stokes shifts. The broad emission is attributed to the self-trapped excitons (STEs), and the narrow band is attributed to the free excitons (Figure 5c). \[70,108\] Besides, 0D perovskites show totally self-trapped excitons emission (Figure 5d). \[70\] Self-trapped excitons refer to an electron–hole pair bound in the defects, which are from transient lattice deformation. It is noteworthy that STEs are viewed as “excited state defects” because there exists strong exciton-lattice coupling in the excited state. \[106\] Transient absorption spectrum can provide direct identification for self-trapped excitons. \[109\] Self-trapped excitons can be categorized as intrinsic self-trapping and extrinsic self-trapping according to the ways the defects formed. A model using a hard ball as electron or hole and a soft sheet as deformable lattice can depict intrinsic self-trapping and extrinsic self-trapping (Figure 5e). Figure 5e-A shows that the perfect sheet is distorted due to the existence of the hard ball, whereas the sheet can return to its original state in the absence of the hard ball. Figure 5e-B exhibits a different condition that initially distorted sheet exists. Figure 5e-C illustrates that an extrinsic self-trapping is relevant to the local nonuniformity of the lattice. \[109\] Notably, a great deal of researches suggest that the presence of self-trapped state is relevant to the dimension of materials, and low dimensional materials are beneficial to the formation of self-trapped exciton. \[110\] Generally, at low temperatures, weak self-trapped exciton emissions can be seen for 3D halide perovskites. At room temperature, free exciton and self-trapped exciton emissions for 2D and 1D perovskites can be observed. While 0D perovskite structure is a suitable environment to form self-trapped states as a result of the absence of the potential energy barrier between the self-trapped excited states and the free exciton. \[70\] Remarkably, the Huang-Rhys factor can be used to judge the soft crystal nature of materials, and the softer crystal nature could more easily generate the self-trapped exciton emissions. \[111\]

There are several fundamental requirements for other metals to substitute lead in halide perovskites, including the coordination type, ionic valence, and ionic radius. \[112\] Generally, the sixfold coordination is required to form the perovskite structure. Typically, Sn²⁺, Ge²⁺, Bi³⁺, Sb³⁺ all possess sixfold coordination. In addition, the lead-free halide perovskites also must be electrically neutral. In ABX₃ perovskite structure, B should be bivalent. So some typical bivalent ions, such as group 14 metals of Sn²⁺ and Ge²⁺ are the excellent candidates. \[111,113\] Notably, two bivalent B²⁺ can be substituted by B⁴⁺ and B⁶⁺ to form halide double perovskites, or vacancy and B⁴⁺ to form vacancy-ordered
Figure 5. a) Direct band-edge emission mechanism for 3D perovskites. b) Quasi-2D multiphase perovskite materials with different $n$ values channel energy which concentrate to smallest bandgap emitters. Reproduced with permission.\[107\] Copyright 2016, Springer Nature. c) Mechanism of free exciton and self-trapped exciton emission in corrugated 2D, and 1D perovskites. d) Mechanism for emission from a reorganized excited state in 0D perovskites. a,c,d) Reproduced with permission.\[170\] Copyright 2017, American Chemical Society. e) Exciton intrinsic self-trapping and exciton extrinsic self-trapping presented by a sheet and hard ball model. Reproduced with permission.\[109b\] Copyright 2018, American Chemical Society.

halide double perovskites.\[66\] In some perovskite derivatives, B can also be trivalent, like group 15 metals of Bi$_3^{3+}$ and Sb$_3^{3+}$.\[38,66b\] Notably, some possible substitutes of lead element have been demonstrated in Figure 1. Especially, the ionic radius is also a significant factor, determining the stability and symmetry of the perovskite structure. The ionic radius of Pb$^{2+}$ is 1.19 Å, and lead in perovskites can be substituted by several metal elements with similar ionic radius, including Sn$^{2+}$ (1.02 Å), Ge$^{2+}$ (0.73 Å), Bi$^{3+}$ (1.03 Å), Sb$^{3+}$ (0.76 Å), and Sn$^{4+}$ (0.69 Å), according to the Goldschmidt’s tolerance factor ($t$).\[114\] In the following sections, the optical and optoelectronic properties of lead replaced by the above-mentioned metals will be deeply discussed.

4.1. Sn-Based Halide Perovskites

Tin (Sn) and Pb are in the same group of the periodic table, and Sn has some similar properties to Pb, including similar ion radii (119 pm for Pb$^{2+}$ and 112 pm for Sn$^{2+}$). Hence, Sn is a preferential element for lead-free halide perovskites. Remarkably, Sn is less much toxic than Pb. Unfortunately, Sn$^{2+}$ is prone to oxidation forming its tetravalent state, which leads to a high defect density and generates trap states, thereby lowering the radiative recombination. The P-type self-doping can be introduced in decomposed materials as a result of the presence of Sn$^{4+}$. The phenomenon of self-doping will lead to perovskite materials with metal-like properties, which is unfavorable for device performance. More specifically, Mitzi et al. manifested that low-dimensional Sn-based halide perovskites could efficiently suppress the metallic conductivity of 3D organic tin halide perovskites.\[75\] Sn-based halide perovskites with different dimensions at the molecular level have been applied widely to photovoltaics, field-effect transistors, LEDs, lasers and photocatalysis.\[115\] Herein, we summarize the structural and optical properties of Sn-based halide perovskites with different dimensionalities.

4.1.1. 3D Sn-Based Halide Perovskites

3D Sn-based halide perovskites were first synthesized in 1974 for CsSnX$_3$ single crystals.\[116\] Later on, Sn-based halide perovskite materials in the form of thin films and other bulk materials were intensively synthesized and investigated, especially for solar cell applications. Considerable research efforts have been devoted to the PL behaviors of 3D Sn-based halide perovskites. At room temperature, solid-state MASnI$_3$ with a direct bandgap shows a strong PL emission at 950 nm, which corresponds to
the onset of the absorption edge.\cite{16b} MA was substituted by ethylenediammonium (en) and formamidinium (FA) to form new materials. Their thin films displayed different emission wavelengths at about 870, 840, and 760 nm with 0, 10, and 25% en/FA ratio. The introduction of en opened up a new bandgap tuning mechanism that originated from massive Schottky style defects.\cite{117} As shown in Figure 6a, the absorbance and steady-state PL of all-inorganic CsSnX3 (X = Cl, Cl0.5Br0.5, Br, Br0.5I0.5, or I) perovskite nanocrystals were demonstrated. The spectra can be adjusted from visible to near-infrared by changing the halogens. The PL mechanism is assigned to a fast band-edge emission and a slow radiative recombination at shallow intrinsic defect sites.\cite{33b} An early research also confirmed that the formation energy of defects was so low (250 meV) that presented high defect densities.\cite{118} Chen et al. showed that CsSnX3 quantum rods synthesized via a simple solvothermal method showed composition-tunable PL from 625 to 709 nm with a FWHM of 32 nm under the excitation of 532 nm.\cite{119} Interestingly, CsSnBr3 hollow nanocages synthesized by the hot injection method presented an absorption onset at 655 nm and PL emission at 685 nm.\cite{120} Wu et al. demonstrated that the substitution of B site in CsSnCl3 nanocrystals and thin films with In3+ or Mn2+ ions displayed cyan (484 nm) and red emission colors (645 nm), respectively. The PL mechanisms were ascribed to B-site vacancies and the energy transfer between CsSn0.9Cl3 and Mn2+, respectively.\cite{121} It was also demonstrated that the oxidation of Sn2+ to Sn4+ was suppressed to a large extent in virtue of reducing agents.\cite{122} To address the stability of Sn4+ essentially, Sn4+-based...
CsSnI₄ nanocrystals with different morphologies were synthesized via a simple phosphine-free hot-injection method. The emission peak at 620 nm did not shift under different excitation wavelengths, as shown in Figure 6b, which suggested that the emission was originated from CsSnI₄ nanocrystals. Han et al. reported that CsₓSnₓXₚ₊₁ (X = Br and I) applied to photodetectors showed two PL peaks at 673 and 870 nm. It can be seen from Figure 6c that CsSnCl₃:Bi⁺ materials are blue phosphors with a photoluminescence quantum yield (PLQY) of 78.9%, which is comparable with blue-emitting lead halide perovskites. CsSnCl₃ is a nonluminous material, and the bandgap decreases with Bi⁺ doping. Density functional theory (DFT) suggests that the thermodynamically preferred [BiSnₓVaClₓ] defects are accounted for the optical absorption and blue emission. And the electronic band structure confirmed the valence band of Bi⁺ doped CsSnCl₃ consisted of Bi 6s and Cl 2p orbitals.

4.1.2 2D Sn-Based Halide Perovskites

In 1993, Papavassiliou et al. synthesized PEA₂SnI₄ and PEA₂SnBr₂ 2D halide perovskites. Subsequently, Mitzi et al. displayed <100>-oriented (C₄H₉NH₃)₂(CH₃NH₃)SnI₃₋₁Sn₁₋ₓIₓ layered halide perovskites and single crystals of <110>-oriented (NH₂Cl)(NH₂)₂(CH₃NH₃)₂SnI₃₋₁Sn₁₋ₓIₓ SnI₃₋₁Sn₁₋ₓIₓ layered perovskites. These researches demonstrated that the choices of different organic cations could lead to different crystallographic orientations of the perovskite sheets. In recent years, 2D halide perovskites have become a striking research spotlight. It is noteworthy that low-dimensional Sn-based halide perovskites exhibit remarkably enhanced air stability in comparison with their 3D counterparts. (OAm)₁SnBr₂ 2D layered perovskites showed bright orange emission centered at 620 nm with PLQY of 88% and FWHM of 140 nm (Figure 6d). It is worth noting that 2D layered (OCTAm)₁SnX₁ (OCTAm = octylammonium cation) synthesized in aqueous phase has a high absolute PLQY of near-unity in the solid-state with PL emission centered at 600 nm and a broad bandwidth of 136 nm. These broad emission is attributed to the self-trapped state emission of tin-layered perovskites. However, for display applications, narrow band emissions are preferred to obtain high color purity. Weidman et al. reported n = 1 and n = 2 (n refers to the layers of metal halide octahedra) Sn-based 2D perovskite nanodisks with narrow band emissions. Strongly coupled 2D Sn-based halide perovskite nanodisks demonstrated an emission at 640 nm, with a PLQY of 6.40 ± 0.14% and FWHM as small as 36 nm. Moreover, the investigation also suggested that aliphatic carboxylic acid was found to play a crucial role in reducing the tin perovskite defect density, thereby improving the emission intensity and stability of tin halide perovskite nanoparticles.

XRD with a periodic diffraction pattern in Figure 6e confirmed the 2D structure of (PEA)₁SnBrₓ thin films. (PEA)₁SnBrₓ were deposited under inert atmosphere and showed superior PL properties with the tunable wavelengths from 650 to 450 nm by adjusting the I/Br ratio (Figure 6f). Chi’s group reported a series of 2D layered Sn-based perovskites to unveil the effects of dielectric confinement on PL. Figure 6g shows the absorption and PL spectra of 2D Sn-based halide with different A sites. Especially, as shown in Figure 6h, the PLQY of 2D Sn-based perovskites with different A sites varied linearly with the (εn)², which can ascribe to the impact of the exciton binding energy. In the formula Eₓ = 4(εn)²Eₓ, the εₓ and εₙ are the dielectric constants of inorganic and organic layers, respectively. Eₓ and Eₙ are the exciton binding energies of 2D halide perovskite and corresponding 3D halide perovskite, respectively. According to this formula, we know that the dielectric constants of inorganic layers and organic layers have an influence on the exciton binding energy of 2D halide perovskites. The dielectric confinement using different aromatic organic cations was confirmed in the investigation. Furthermore, the research demonstrated that nanoscale TEA₂SnI₄ (TEA = thienylethylamine) layered perovskites showed a record high PLQY of 21% with FWHM of 32 nm.

4.1.3 1D and 0D Sn Based Perovskites

In addition to the 2D Sn-based halide perovskites, 1D and 0D Sn-based halide perovskites have also been studied recently. Crystals of 0D (C₄N₂H₁₄X)₄SnX₆ (X = Br, I) and 1D (C₄N₂H₁₄X)₄SnBr₄ were synthesized. The synthesized 1D (C₄N₂H₁₄X)₄SnBr₄ showed no PL and underwent a structural transformation under UV excitation to 0D (C₄N₂H₁₄X)₄SnBr₄ with a bright yellow emission. The 0D (C₄N₂H₁₄X)₄SnBr₄ showed excellent optical properties with a near-unity PLQY. 0D Sn-based perovskites possessed superior photostability in the ambient, because the PL centers were protected completely by the organic shells. All-inorganic 0D CsSnBr₆ perovskites with a PL emission at 540 nm and a PLQY of 15 ± 5% were synthesized. And a series of 0D CsSnₐ₋ₐ₋₁Sn(Iₓ₋ₓ)ᵢₖ (A = K⁺, Cs⁺) materials were also prepared and manifested the emission wavelength from 500 to 620 nm. As illustrated in Figure 6i, the PL mechanism of full inorganic 0D Sn-based halide perovskites is ascribed to self-trapping exciton emission. And the insets demonstrate that the HOMO (valence band) consists of Sn 5p and Br 5p orbitals, and LUMO (conduction band) consists of Sn 5s and Br 5p orbitals. In addition to the low-dimensional Sn-based halide perovskites, there are some nonperovskite structure Sn-based halide materials reported. Morad et al. presented highly emissive single crystals of 0D disphenoidal Bmpip₂SnBr₄ and Bmpip₂SnI₄ (Bmpip = 1-buty-1-methylpiperidinium; C₁₀H₁₄N₂) with emission peaks at 666 and 730 nm, respectively. In addition, Bmpip₂SnBr₄ also displayed intense emission under X-ray excitation, which was comparable with the commercial inorganic X-ray scintillator. Recently, Kanatzidis’ group synthesized 1D (DAO)₂SnI₆ (DAO = 1:8-octylammonium) single crystals and thin films. (DAO)₂SnI₆ thin films with a PLQY of 36% demonstrated superior water stability, which could resist water for more than 15 h.

The above discussion suggests that Sn-based halide perovskites have made great advances in solar cells, light-emitting devices, and X-ray photodetectors over the past several years. As for Sn-based perovskite light-emitting materials, ultrabroad band PL emission with high PLQY is suitable for white-light LED application. However, narrowband PL emission is not satisfactory. Instability and low PLQY are two significantly challenging issues. Notably, Sn-based halide perovskites have a great potential in infrared light emission, which deserves more attention. In order to
4.2. Ge-Based Halide Perovskites

Germanium (Ge) is in the same group of lead (Pb) and tin (Sn) and has less toxicity than Pb, but more toxic than Sn. It is also considered as a potential candidate. However, Ge$^{2+}$ is prone to be oxidized to Ge$^{4+}$ owing to the active 4s lone pair electrons. There are quite a few reports about Ge-based halide perovskites. Mhaisalkar’s group reported Ge-based halide perovskites, including three AGeI$_3$ (A = Cs$^+$, MA$^+$, FA$^+$) materials with R3m space group symmetry. The bandgaps of AGeI$_3$ were 1.63, 2.0, and 2.35 eV for CsGeI$_3$, MAGeI$_3$, and FAGEI$_3$. Mitzi synthesized single crystals of 2D (C$_x$H$_y$NH$_z$)$_2$GeI$_4$ and studied the PL properties. The (C$_x$H$_y$NH$_z$)$_2$GeI$_4$ had a weak emission peak at 690 nm with a FWHM of 180 nm. The 2D layered (PEA)$_2$Ge$_2$I$_5$, SnI$_4$ (x ≤ 0.5) with direct bandgap showed emission peaks at wavelengths of 613 (x = 0), 628 (x = 0.125), 642 (x = 0.25), and 655 nm (x = 0.5) at room temperature. With the increase of Sn, the emission FWHM decreases possibly due to a more pronounced distortion of [GeI$_6$]$^{4-}$ octahedra than [SnI$_6$]$^{4-}$ octahedra. Time-resolved PL suggested that there were two processes: charge-carrier trapping for short-lifetime and exciton recombinaction for long-lifetime. Sadhanala’s group presented Ge-based and Sn-based halide solid solutions and demonstrated the emission wavelength from 640 to 945 nm with a PLQY from 100% to 0. Single crystals of disphenoidal OD Bmpip$_2$GeBr$_4$ were prepared with a red emission of 670 nm and a large Stokes shift of 330 nm.

Recently, Yang’s group identified 23 lead-free halide perovskites for light-emitting diodes via high-throughput computational design, including (MA)$_2$GeBr$_4$, (MA)$_2$GeI$_4$, (AD)$_2$GeI$_4$ (AD = (CH$_2$)$_3$NH$_2$), which provides a new direction to develop new-type lead-free halide perovskites. Researchers can seek for suitable synthesis method to prepare the proposed Ge-based halide perovskites and study relevant optical and optoelectrical properties. Combining theory with experiment will greatly promote the development of lead-free perovskite optoelectronics.

4.3. Bi-Based Halide Perovskites

Lead-based halide perovskites present superior optoelectrical characteristics, which are strongly relevant to the 6s$^2$6p$^0$ electronic configuration of Pb$^{2+}$. However, only three stable cations have the 6s$^2$6p$^0$ electronic configuration, namely, Ti$^4+$, Pb$^{2+}$, and Bi$^{3+}$. Among these, only Bi$^{3+}$ ions have relatively low toxicity, which promotes Bi-based halide perovskites to be a valid alternative. Additionally, Bi-based halide perovskites were identified as defect-tolerant semiconductors via computational screening. Among Bi-based halide perovskites, a common formula is A$_2$Bi$_x$I$_y$, where A stands for Cs$^+$, Rb$^+$ or MA$^+$ and X refers to halogen anion Cl$^-$, Br$^-$ and I$^-$. At the molecular level, there are different dimensionalities for A$_2$Bi$_x$I$_y$ according to various connection types between the adjacent Bi-based halide octahedra.

Tang’s group reported that single crystals and nanocrystals of MA$_3$Bi$_2$Br$_9$ were synthesized by evaporating the solvent of the saturated solution and collaborative solvent ligand-assisted precipitation (Co-LARP), respectively. The MA$_3$Bi$_2$Br$_9$ nanocrystals with an average diameter of 3.05 nm showed an emission peak around 423 nm with FWHM of 62 nm as shown in Figure 7c, manifesting a huge blue-shift (compared to the single crystals) due to quantum confinement effect. Afterwards, the optical properties of Cl$^-$ anion passivated MA$_3$Bi$_2$Br$_9$ nanocrystals were studied. As shown in Figure 7d, a significant boost of PLQY (54.1%) was observed where the surface defects were suppressed effectively. Time-resolved PL measurements with a monoexponential fitting and temperature-related PL showing larger exciton binding energy verified the superior passivation effect. In general, the all-inorganic halide perovskites have better stability than the organic–inorganic hybrid halide perovskites, because organic cations are vulnerable to decomposition. Correspondingly, all-inorganic Cs$_3$Bi$_2$X$_9$ nanocrystals were also prepared by Tang’s group and Han’s group. Tang’s group utilized ethanol as the main solvent to prepare Cs$_3$Bi$_2$X$_9$ nanocrystals, which displayed a blue emission at 410 nm with a PLQY of 19.4% and a superior stability. Notably, the Cs$_3$Bi$_2$Br$_9$ nanocrystals displayed a significant PL enhancement after some amount of water was added into the ethanol solution containing nanocrystals. The phenomenon was ascribed to the passivation effect of BiOBr. The effect of coordinating H$_2$O in lead-free halide perovskites was also studied. In addition to decomposition, water also influenced the crystallization of perovskites. Zhang et al. reported that suitable amount of water improved the PLQY of perovskites and changed the size and shape of perovskite nanocrystals. Han’s group synthesized Cs$_3$Bi$_2$X$_9$ nanocrystals using DMSO as solvent and
isopropanol as the antisolvent via a simple and scalable synthesis method, exhibiting a tunable emission wavelength though composition adjustment as shown in Figure 7e.\textsuperscript{[144]} Besides, Han’s group carried out the transient absorption measurement and the time-resolve PL in the Cs$_3$Bi$_2$Br$_9$ nanocrystals, which provided an extensive comprehension on the charge-carrier dynamics involving both radiative and non-radiative processes.

Excited state dynamics of ligand-free Cs$_3$Bi$_2$Br$_9$ nanocrystals suggested that Auger recombination and charge transfer from excited states to trapping states took place in 2–20 ps, intrinsic radiative combination happened at 300 ps, and the decay of the long-lived trapping states occurred at more than 3 ns as shown in Figure 7f. Excited state dynamic process is responsible for the low PLQY of the ligand-free Cs$_3$Bi$_2$Br$_9$ nanocrystals. Additionally, the ultrafast component greatly decreased in the OA capped Cs$_3$Bi$_2$Br$_9$ NCs, which suggested that Cs$_3$Bi$_2$Br$_9$ nanocrystals could be passivated effectively via the use of oleic acid as the surfactant.\textsuperscript{[144]}

The broad PL of single crystals of 2D Rb$_3$Bi$_2$I$_9$ and Cs$_3$Bi$_2$I$_9$ was observed at room temperature, which was ascribed to inducing small polarons and resulting in trapping of excitons by the lattice. Moreover, the similar effective phonon energy was obtained by temperature-dependence PL and Raman spectra. Rb$_3$Bi$_2$I$_9$ and Cs$_3$Bi$_2$I$_9$ presented high resistivity and high photoresponse under the laser photoexcitation, which demonstrated their potentials in detector applications.\textsuperscript{[146]}

Figure 7. a) 2D crystal structure of Cs$_3$Bi$_2$X$_9$ was displayed viewed down the b-axis and c-axis. Reproduced with permission.\textsuperscript{[154]} Copyright 2019, American Chemical Society. b) OD Bi-based halide perovskite structure consists of diocathedra face-sharing (Bi$_2$X$_9$)$_3^-$ clusters with hexagonal phase. Reproduced with permission.\textsuperscript{[147]} Copyright 2016, Wiley-VCH. c) Absorption and PL spectra of MA$_3$Bi$_2$Br$_9$ nanocrystals. Reproduced with permission.\textsuperscript{[143]} Copyright 2018, American Chemical Society. d) Photographs of MA$_3$Bi$_2$Br$_9$ nanocrystal solutions passivated with different amount of Cl$^-$ under a 325 nm UV lamp excitation. Reproduced with permission.\textsuperscript{[147]} Copyright 2015, Wiley-VCH. e) Photographs (top) and steady-state absorption and PL spectra (bottom) of colloidal Cs$_3$Bi$_2$I$_9$ (X = Cl, Br$_{0.5}$I$_{0.5}$) nanocrystals. f) Excited dynamics model of Cs$_3$Bi$_2$Br$_9$ nanocrystals via combining time-resolved PL and transient absorption. Reproduced with permission.\textsuperscript{[144]} Copyright 2017, Wiley-VCH. g) PL spectra for the Cs$_3$Bi$_2$I$_9$, MA$_3$Bi$_2$I$_9$ and MA$_3$Bi$_2$I$_9$Cl$_x$ thin films. Reproduced with permission.\textsuperscript{[147]} Copyright 2015, Wiley-VCH. h) Normalized absorption and PL spectra of Cs$_3$Bi$_2$I$_9$ colloidal nanocrystals. i) Proposed recombination process in Cs$_3$Bi$_2$I$_9$ nanocrystals. Reproduced with permission.\textsuperscript{[152]} Copyright 2017, American Chemical Society.
4.3.2. 0D Bi-Based Halide Perovskites

In 2015, thin films of 0D Bi-based halide perovskite were synthesized by Park et al. 0D Cs$_5$Bi$_3$I$_9$ with larger exciton binding energy of 270 meV displayed strong PL (Figure 7g). The nanocrystals had a hexagonal P63/mmc space group and exhibited broad PL emission, which was attributed to free excitons and defect emission. Strikingly, two peaks in the PL spectra of Cs$_5$Bi$_3$I$_9$ nanocrystals were observed at 580 nm (2.14 eV) and 605 nm (2.05 eV) (Figure 7h). The inset shows the morphology. Moreover, early investigations revealed that the direct bandgap transition and indirect bandgap transition had vastly different behaviors with the increasing temperature in theory. Generally, the radiative recombination via direct bandgap transition decreases with rising temperature due to the thermal quenching effect. On the contrary, the radiative recombination through indirect bandgap transition can be boosted with elevated temperature, which is ascribed to the additional momentum compensation from phonons to obey the momentum conservation. The two different phenomena were indeed observed. Furthermore, DFT calculations shown the presence of direct and indirect bandgaps. In addition, the relevant PL mechanism (Figure 7i) is that the electrons in the valence band jump to the conduction band under excitation involving the direct bandgap transition, as shown in the absorption spectra. With the help of phonons, the indirect bandgap transition and direct bandgap transition occurred corresponding to the 605 and 580 nm emission.

Intriguingly, mixed halides contribute to the molecular dimensionality transformation from 0D Cs$_5$Bi$_3$I$_9$ to 2D Cs$_5$Bi$_3$I$_9$Cl$_1$, and this phenomenon highlights the importance of interlayer interactions in the defect perovskite family. Song’s group reported a new kind of Bi-based perovskite, namely, Rb$_7$Bi$_3$Cl$_16$, in the form of single crystals and nanocrystals. Rb$_7$Bi$_3$Cl$_16$ had a special crystal structure, which displayed as a 0D cluster composed of two kinds of octahedra with different distortions. Rb$_7$Bi$_3$Cl$_16$ nanocrystals with an average diameter of 1.85 nm exhibited a blue emission at 437 nm with PLQY of 28.43% and FWHM of 46 nm, providing a direction to develop new lead-free halide perovskites.

Compared with Sn-based and Ge-based halide perovskites, Bi-based halide perovskites possess superior stability. Remarkably, Bi-based halide perovskites belong to defect-tolerant perovskites. In terms of the currently developed Bi-based halide perovskites, most of them are low-dimension perovskites. As light-emitting materials, low-dimension perovskites have larger exciton binding energies, which is beneficial for exciton recombination to obtain higher PLQY. However, low-dimension perovskites generally possess inferior carrier transport, which is detrimental in optoelectrical applications. There are several challenges for Bi-based halide perovskite materials. First, their structure–property relationships and underlying mechanisms are extremely unclear. Second, Bi-based halide perovskites with direct bandgap are scarce, which can be obtained via experimental tools and theoretical calculations. Third, the thin film quality of Bi-based halide perovskites needs to be improved. Some common methods can be attempted, including optimizing the precursor solution, solvent-engineering to decrease the volatility of the precursor solutions and their rapid crystallization.

4.4. Sb-Based Halide Perovskites

It is reasonable to substitute Pb$^{2+}$ ions in perovskite structure by antimony (Sb) apart from Sn, Ge, and Bi elements. Structurally, stable A$_3$Sb$_3$X$_9$ can be derived from 2/3 occupancy of the B sites in the A$_3$B$_3$X$_9$ perovskite, which can be considered as "defect perovskites." There are two perovskite phases, including 0D dimer form (space group P63/mmc, No. 194) and 2D layered form (space group P3m1, No. 164), which can be formed depending on the synthesis conditions. The 0D dimer phase perovskites consist of dioctahedral face-sharing (Sb$_3$X$_9$)$^{1/2-}$ clusters, which can be synthesized via a low-temperature solution process (Figure 8a). The 2D perovskites consist of corrugated layer structure with partially corner-sharing MX$_6$ octahedra, which are usually thermodynamically unstable (Figure 8b). The change in dimensionality has a huge influence on the optical and electronic properties of perovskite materials.

4.4.1. 2D Sb-Based Halide Perovskites

2D colloidal Cs$_5$Sb$_3$I$_9$ and Rb$_7$Sb$_3$I$_9$ nanocrystals synthesized by the hot injection method were studied. The Cs$_5$Sb$_3$I$_9$ nanoplates and Cs$_5$Sb$_3$I$_9$ nanorods can be derived from different reaction temperatures. As shown in Figure 8c, the Cs$_5$Sb$_3$I$_9$ nanoplates display an XRD pattern with periodic property, which confirms that the materials belong to the 2D structure. The PL lifetime measurements provided some valuable information about Cs$_5$Sb$_3$I$_9$ nanoparticles and nanorods, wherein the nonradiative decay with lifetimes of about 1 ns decreased the PL efficiency to about 5%. The underlying reason is the deep defect levels in Cs$_5$Sb$_3$I$_9$ possibly originated from both localization and reduction of the spin–orbit splitting of Sb 5p-orbital. The single crystals and quantum dots of Cs$_5$Sb$_3$Br$_3$ were prepared. <111>-stacked 2D layered Cs$_5$Sb$_3$Br$_3$ nanocrystals exhibited remarkable optical properties, including blue emission at 410 nm, PLQY of 46%, FWHM of 41 nm and tunable emission wavelength from 370 to 560 nm via anion exchange reactions (Figure 8d,e). The excellent optical characteristics were mainly attributed to two aspects. On the one hand, Br-rich surface passivated the defects of Cs$_5$Sb$_3$Br$_3$ nanocrystals; on the other hand, larger exciton binding energy of 530 meV demonstrated more efficient exciton radiative recombination. Zuo et al. reported that (NH$_4$)$_3$Sb$_2$I$_9$Br$_6$ single crystals and thin films were synthesized by antisolvent vapor-assisted crystallization method (AVC) and spin-coating method, respectively. The (NH$_4$)$_3$Sb$_2$I$_9$ single crystals demonstrated an absorption onset at 645 nm and a PL emission at 639 nm. Whereas the uniform and compact thin films of (NH$_4$)$_3$Sb$_2$I$_9$Br$_6$ presented an absorption onset at 558 nm. The 87 nm blue shift phenomenon was also observed in lead halide perovskite single crystals and thin films, which indicates that the excitons dissociate to free charges at room temperature. Recently, Chu’s team presented 2D layered Cs$_5$Sb$_3$I$_9$ thin films for LEDs. 2D layered Cs$_5$Sb$_3$I$_9$ thin films with direct bandgap showed an emission peak at 750 nm with a FWHM of 120 nm and tunable emission wavelengths as shown in Figure 8f. A model explained these broad emissions, where the interactions between radiative transitions and phonons are presented, as shown in Figure 8g. Absorption transition occurs between...
energy levels 1 and 2, and the emission transition happens from energy 3 to energy 4 after lattice interaction with phonons.\cite{156}

4.4.2. 0D Sb-Based Halide Perovskites

In addition to the 2D Sb-based halide perovskites, 0D Sb-based halide perovskites are also widely studied. The fabricated 0D (CH₃NH₃)₃Sb₂I₉ thin films showed a PL emission at 1.58 eV.\cite{157} The 0D mixed Sb- and Bi-based perovskite single crystals of (C₈NH₁₂)₄Bi₀.₅₇Sb₀.₄₃Br₇∙H₂O synthesized by a solution process demonstrated an ultrabroadband emission spectrum from 400 to 850 nm, which was attributed to the combination of free excitons and self-trapped excitons.\cite{78} Recently, 0D Sb-based halide hybrid materials with pyramidal SbCl₅ structure also show superior optical characteristics. The single crystals of 0D (C₉NH₂₀)₂SbCl₅ show a PL emission at 590 nm, an extremely high PLQY of close to unity and a wide FWHM of 119 nm, which is attributed to exciton self-trapping.\cite{132} As shown in Figure 8h, 0D (Ph₄P)₂SbCl₅ bulk single crystals with high thermostability and photostability also demonstrated superior optical characteristics including a PLQY of 87%, a broad red emission at 648 nm and a phosphorescent lifetime of 4.57 ± 0.09 µs. In addition, theory calculations explained that a stronger excited state distortion from a shorter Sb–Cl bond led to a larger Stoke shift of (Ph₄P)₂SbCl₅ (273 nm) than (C₉NH₂₀)₂SbCl₅ (210 nm).\cite{82}

Currently reported Sb-based halide perovskites are summarized. There are some prospects and challenges for Sb-based halide perovskites. 0D Sb-based halides bulk crystals with high PLQY and larger Stoke shift demonstrate outstanding potentials in WLED lighting and X-ray scintillator. Recently, Ma et al. adopted a modified recrystallization method to obtain a PLQY of 51.2%, which gives us an idea to optimize the synthesized lead-free halide perovskites to gain superior performance.\cite{66b} Above optimization needs us to understand the source of the defects. The challenges lie in the following aspects. On the one hand, Sb-based halide perovskites serve as “defect perovskites,” and there are indeed high contents of deep-level defects in the A₃B₂X₉ structure. On the other hand, Sb-based halide perovskites still have the problem of poor morphology. Seeking suitable synthesis methods to obtain high-quality Sb-based halide thin films is necessary.\cite{156}

4.5. Halide Double Perovskites

Recently, the halide double perovskites with a formula of A₂M⁺M₃⁺X₆ (A = Cs⁺, MA⁺; M⁺ = Ag⁺, Na⁺, In⁺; M₃⁺ = In³⁺, Bi³⁺, Sb³⁺; X = Cl⁻, Br⁻, I⁻) and the possible element substitutes are presented in Figure 1. Halide double perovskites have gained widespread interest as candidates for lead-free halide perovskite materials, owing to superior stability against light, heat, and moisture. In fact, the double perovskite structure is also named elpasolite, which is known for its ferroelectric properties since the 1960s. However, the photoelectronic properties of halide double perovskites were only recently investigated. Typically, halide double perovskites present 3D structure at the molecular level, wherein [M⁺X₆] and [M₃⁺X₆] corner-sharing octahedra...
Figure 9. a) Crystal structure of halide double perovskites. Reproduced with permission. Copyright 2018, Wiley-VCH. b) The band structure and bandgaps of Cs$_2$AgInCl$_6$ calculated by HSE hybrid functional (blue and red lines) and PBE0 functional (shaded area). The maximum of valence band is set to the energy zero. Reproduced with permission. Copyright 2018, Wiley-VCH. c) PL spectra of Mn$^{2+}$ doped Cs$_2$AgInCl$_6$ samples with different contents under 340 nm excitation. Inset: images of luminescence of powder under UV excitation. Reproduced with permission. Copyright 2018, Royal Society of Chemistry. d) Calculated photoluminescence spectrum and experimental photoluminescence spectrum of Cs$_2$AgInCl$_6$. Reproduced with permission. Copyright 2018, Springer Nature. e) Steady-state absorption spectra of ligand-free and OA-capped Cs$_2$AgBiBr$_6$ nanocrystals. Reproduced with permission. Copyright 2018, Wiley-VCH. f) Schematic representation of the change of bandgap type with different In$^{3+}$/Bi$^{3+}$ ratio and corresponding PLQY. Inset: PL image of ligand-free Cs$_2$Ag(In$_{1-x}$Bi$_x$)Cl$_6$ ($x = 0, 0.25, 0.5, 0.75,$ and $0.9$) nanocrystals under UV light of 365 nm. Reproduced with permission. Copyright 2018, American Chemical Society. g) Single-crystal X-ray structures (298 K) of the (001) layered double perovskites (BA)$_4$AgBiBr$_8$. Orange, white, turquoise, brown, blue, and gray spheres represent Bi, Ag, Cs, Br, N, and C atoms, respectively and H atom is omitted for clarity. Reproduced with permission. Copyright 2018, American Chemical Society. h) Absorption (pink) and emission (blue) spectra for (BA)$_4$AgBiBr$_8$ at 2.5 GPa. Reproduced with permission. Copyright 2019, Wiley-VCH.

are alternately arranged (Figure 9a). There are a large number of halide double perovskite materials, including single crystals, thin films, and nanocrystals for different photoelectronic applications such as light-emitting diodes, solar cells, photodetectors, X-ray detectors. 

In 2016, many research groups reported the synthesis of Cs$_2$AgBiX$_6$ (X = Cl, Br, I) double perovskite materials via solid-state reaction and solution process. The cubic Cs$_2$AgBiBr$_6$ powders with a space group $Fd-3m$ were obtained by Karunadasa’s group, which displayed a weak PL emission at 1.87 eV at room temperature. Greul et al. reported that the Cs$_2$AgBiBr$_6$ thin films had a broad PL with low PLQY, which was likely attributed to the nonradiative defect effect. 

The band structure calculations and optical measurements suggested that Cs$_2$AgBiBr$_6$ and Cs$_2$AgBiCl$_6$ belonged to indirect bandgap semiconductors, which are not ideal for solar cells and light-emitting applications. Notably, a novel halide double perovskite Cs$_2$AgInCl$_6$ with direct bandgap was demonstrated by Volonakis et al. in 2017. In Figure 9b, density functional theory (DFT) indicated that the conduction band of Cs$_2$AgInCl$_6$ originated from Cl-3p and In-5s/Ag-5s states, and the valence band was attributed to Cl-3p and In-4d/Ag-4d states. Moreover, Cs$_2$AgInCl$_6$ powders demonstrated a PL emission at 608 nm with FWHM of 120 nm. Simultaneously, the investigation of bandgap engineering was also carried out in halide double perovskites. In the trivalent metals alloyed Cs$_2$AgBiBr$_6$ system, the bandgap of Cs$_2$AgBiBr$_6$ can be enlarged by increasing the contents of In$^{3+}$ in the Cs$_2$AgBi$_{1-x}$In$_x$Br$_6$, whereas the bandgap decreased via increasing the contents of Sb$^{3+}$ in the Cs$_2$AgBi$_{1-x}$Sb$_x$Br$_6$. 

Afterwards, Mn$^{2+}$ doped halide double perovskites were presented. Mn$^{2+}$ doped Cs$_2$AgInCl$_6$ double perovskite emitted red light under UV excitation, as shown in Figure 9c. It is worth mentioning that Cs$_2$Ag$_{0.6}$Na$_{0.4}$InCl$_6$:0.04Bi$^{3+}$ synthesized by hydrothermal method demonstrated stable emission of warm white light (460–700 nm) with PLQY of $86 \pm 3\%$ and the broad-band emission of Cs$_2$AgInCl$_6$ originates from self-trapped excitons (STEs) as shown in Figure 9d, which was confirmed experimentally and theoretically. The excitation spectra presented similar shapes and features under the emission from 460 to 700 nm in Cs$_2$Ag$_{0.6}$Na$_{0.4}$InCl$_6$:0.04Bi$^{3+}$, suggesting that white emission is originated from the same excited state. Moreover, the PLQY was independent of the excitation power, meaning that the white emission was not attributed to the permanent defects. In addition, the transient absorption spectra further directly verified the presence of STEs. These experimental results were consistent with the calculation results of exciton self-trapping time in theory. In this system, the roles of Na$^+$ are to break the parity-forbidden transition and reduce electronic dimensionality, which results in efficient white emission via radiative recombination of STEs. And the roles of Bi$^{3+}$ are considered to improve the crystal perfection and localized exciton. Subsequently, alkali-metal ions Li$^+$ and...
K⁺ have also been introduced to the Cs₂AgInCl₆ NCs, modifying the white-light emission.⁷¹

Over a span of less than two years, a large number of colloidal nanocrystals of halide double perovskite has been synthesized.⁸⁸-⁹⁸ The ligand-free Cs₂AgBiBr₆ nanocrystals with an average diameter of 5.0 nm demonstrated an excitation absorption peak at 440 nm with a long absorption tail up to 700 nm. The absorption tail means the existence of a transition involving sub-bandgap states, which may attribute to the defect states of nanocrystals. As shown in Figure 9e, we can observe that the tail phenomenon is suppressed in the oleic acid capped halide double perovskite nanocrystals. The phenomenon suggested that oleic acid can serve as the surfactant to passivate the defects in Cs₂AgBiCl₆ nanocrystals, thus increasing PLQY.⁸² Manna’s group first reported colloidal Cs₂AgInCl₆ nanocrystals and Mn²⁺ doped Cs₂AgInCl₆ nanocrystals with good size distributions. Cs₂AgInCl₆ nanocrystals displayed a broad white-emitting PL with a PLQY of ≈1.6 ± 1%, and a higher PLQY of ≈16 ± 4% was obtained in orange-emitting Mn³⁺ doped Cs₂AgInCl₆ nanocrystals.⁶⁶ In addition to Mn³⁺ doping, Bi³⁺ and lanthanide ions (Tb³⁺, Yb³⁺, Er³⁺) doped Cs₂AgInX₆ nanocrystals have also been synthesized and Bi³⁺ doped Cs₂AgInₓBiₓX₆ emitted orange light.⁸⁴ Gao’s group reported that Tb³⁺ doped Cs₂AgInₓBiₓCl₆ nanocrystals. Their emissions could be adjusted from green light to orange light, which was ascribed to the energy transfer channel from self-trapped excitons to Tb³⁺ ions.⁶⁶ Upon Yb³⁺ and Er³⁺ doped, the emissions of 996 nm for Yb³⁺ and 1537 nm for Er³⁺ dopants were observed in Cs₂AgInCl₆ nanocrystals. The introduction of these dopants expands the emission range and facilitates relevant luminescence applications, including optical communication, plant growth, and night-vision devices.⁸⁴-⁹⁷

Interestingly, Han’s group reported Cs₂AgInₓBi₃ₓCl₆ (x = 0, 0.25, 0.5, 0.75, and 0.9) nanocrystals with different bandgap types, including direct bandgap (x = 0.75, 0.9) and indirect bandgap (x = 0, 0.25, 0.5) as shown in Figure 9f. Halide double perovskite nanocrystals with different bandgap types manifest disparate optical features and charge carrier dynamics. Cs₂AgInₓ₋₃BiₓCl₆ and Cs₂AgInₓ₋₃BiₓCl₆ nanocrystals with direct bandgap demonstrated dual-color emission (violet emission of 395 nm and orange emission of 570 nm), whereas Cs₂AgInₓ₋₃Cl₆ nanocrystals (x = 0, 0.25, 0.5) showed only one emission peak (400-410 nm). Femtosecond transient absorption measurements unveiled the essence of radiative and nonradiative processes with different bandgap types. The rapid component of GSB (ground-state bleach) decay is attributed to the intrinsic sub-bandgap trapping. And bleaching signal at long wavelengths originates from the sub-bandgap trap-state absorption and indirect bandgap transition. In Cs₂AgInₓ₋₃BiₓCl₆ nanocrystals, there is only a positive PIA (photoinduced absorption) decay signal observed.⁹²

Recently, Cs₂AgNa₁₋ₓInₓBi₃₋ₓCl₆ nanocrystals are under research spots, which were described by Manna’s group and Tang’s group successively. Manna et al. reported that Bi³⁺ doped Cs₂AgNa₁₋ₓIn₉₋ₓCl₆ nanocrystals synthesized by the hot injection method showed PLQY of 22%. Tang’s group reported that Cs₂AgNa₁₋ₓInₓBi₃₋ₓCl₆ nanocrystals prepared by room temperature recrystallization process displayed a broad emission with PL peak of 557 nm and PLQY of 64%. Meanwhile, the color temperature could be adjusted by changing Na⁺ and Bi³⁺ doping contents.¹⁰⁸ Han’s group synthesized cubic Cs₂NaInCl₆ nanocrystals with a direct bandgap and Ag⁺ doped Cs₂NaInCl₆ nanocrystals. The research demonstrated that Ag⁺ doped Cs₂NaInCl₆ nanocrystals exhibited a broad PL emission peak (centered at 535 nm in a range of 400-750 nm) originating from STEs. That was directly verified by the transient absorption measurements. Furthermore, Ag⁺ doping also improved the stability in comparison with the undoped materials.⁸⁵ Moreover, Mn²⁺ doped Cs₂NaInₓBi₂₋ₓCl₆ (0 ≤ x ≤ 1) NCs were also synthesized, and the emission color could be adjusted from yellow to orange-red, with a PLQY of 44.6%.¹⁶⁹

The above-mentioned halide double perovskites are 3D perovskite structure. Similarly, there are several investigations for 2D halide double perovskites.¹⁷⁰ Mitzi’s team prepared 2D halide double perovskites [AE₂T]₂AgBi₆ (AE₂T = 5,5’-diylbis(aminooethyl)-(2,2’-bithiophene)) which was predicted to be a semiconductor with a direct bandgap. However, [AE₂T]₂AgBi₆ was barely luminescent at room temperature even at 78 K temperature.¹⁷⁰ For (BA)₂AgBiBr₆ (BA = CH3(CH2)₃NH3), as shown in Figure 9g, it displayed a weak and slightly broadened PL at 20 K, which was quenched rapidly upon warming. However, (BA)₂AgBiBr₆ demonstrated obvious PL under the condition of the pressure of 2.5 GPa as shown in Figure 9h.¹⁷⁰a,¹⁷¹ A unique <111>-oriented mixed metal layered perovskite CsₓCuSb₂Cl₁₂ with a direct bandgap was synthesized by Vargas et al., which provides us a new strategy for material design with the various substitutions in the M⁺ and M¹⁺ sites.¹⁷² Besides, 2D vacancy-ordered double perovskites CsₓMnₓBi₂Cl₁₂, CsₓCdₓBi₂Cl₁₂ and CsₓCdₓ₋₁MnxBi₂Cl₁₂ were reported continuously, enriching the family of lead-free halide perovskites.¹⁷³

Halide double perovskites have the flexibility for various compositional adjustments. In the future, the research for lead-free halide double perovskites may direct to the following aspects. Conversion of bandgap type and break of parity-forbidden transition in halide double perovskites by doping or alloying ions deserves further research. In addition, the high-quality thin films can be further explored via different vapor deposition process. Moreover, in order to transport carriers effectively, high electronic dimensionality should be guaranteed.

### 4.6. Cu and Other Metal-Based Halide Perovskites

Currently, Cu-based halide perovskites have received great attention for the abundance, low cost, and environmental friendliness of Cu element. In 2016, Mathews’ group first reported 2D Cu-based perovskites MA₂CuCl₃Brₓ powders and films, which were synthesized by spontaneous crystallization and spin-coating, respectively. These powders’ bandgaps varied with increasing Br contents.¹⁷⁴ Afterwards, Cu-based perovskite materials appeared widely in research. Yang et al. synthesized Cs₂CuX₄ (X = Cl, Br, Br/I) nanocrystals via an improved ligand-assisted recrystallization technique at room temperature. The PL wavelengths of Cs₂CuX₄ nanocrystals with blue-green emitting could be adjusted via the molar ratio of the raw materials as shown in Figure 10a.¹⁷⁵ Notably, monovalent Cu(I)-based materials were also intensively applied to light generation, but they do not belong to perovskite or perovskite analog.
shown in Figure 10b, the unit consists of tetrahedrons instead of octahedra. These materials have excellent optical properties with environmental friendliness.

Saparov’s group reported that the Cs₃Cu₂Br₅₋ₓIₓ phosphors have a maximum emission wavelength from 443 to 455 nm with near-unity PLQY. Jun et al. prepared 0D Cs₃Cu₂I₅ single crystals and thin films via vapor saturation of an antisolvent (VSA) and spin-coating, respectively. A 5 mm Cs₃Cu₂I₅ single crystal showed 445 nm PL emission with high PLQY of 90% and the greatly stable Cs₃Cu₂I₅ thin films displayed 445 nm with high PLQY of 62% as shown in Figure 10c. Afterwards, corresponding nanocrystals were presented. Han’s group reported 0D Cs₃Cu₂I₅ nanocrystals and 1D CsCu₂I₃ nanorods synthesized by the hot injection approach under different temperatures. The 1D CsCu₂I₃ nanorods showed a weak yellow emission positioned at 553 nm with a PLQY of 90% and the greatly stable Cs₃Cu₂I₅ thin films displayed 445 nm with high PLQY of 62% as shown in Figure 10c. Afterwards, corresponding nanocrystals were presented. Han’s group reported 0D Cs₃Cu₂I₅ nanocrystals and 1D CsCu₂I₃ nanorods synthesized by the hot injection approach under different temperatures. The 1D CsCu₂I₃ nanorods showed a weak yellow emission positioned at 553 nm with a PLQY of 90% and the greatly stable Cs₃Cu₂I₅ thin films displayed 445 nm with high PLQY of 62% as shown in Figure 10c. Afterwards, corresponding nanocrystals were presented.

Apart from Cu-based halide materials, there are some other metal-based halide perovskites reported. Cs₂TiBr₆ vacancy-ordered double perovskites thin films synthesized by a facile low-temperature vapor-based method showed bright luminescence centered at 704 nm under the excitation of 395 nm, which was attributed to its band-edge emission. Concurrently, single crystals of Cs₂PdBr₆ vacancy-ordered defect-variant perovskite displayed emission at 772 nm. Lee’s group reported rare-earth-element ytterbium substituted lead-free halide perovskite nanocrystals of CsYbI₃ synthesized by the hot injection method. The cubic perovskite CsYbI₃ nanocrystals exhibited a strong PL at 671 nm as shown in Figure 10f and a high PLQY of 58% under the excitation of 450 nm. Yang’s group synthesized CsEuCl₃ nanocrystals with a blue emission at 435 nm and a narrow FWHM of 19 nm. Among lead-free halide perovskites, CsEuCl₃ possesses the narrowest FWHM, which shows some promise in display applications. The development of CsYbI₃ and CsEuCl₃ inspires new type lead-free halide perovskite materials via rare-earth substitutes. Su’s group reported that red-emitting Cs₂InBr₅·H₂O single-crystal demonstrated a broad emission at 695 nm with a high PLQY of 33% (Figure 10g). Interestingly, Cs₂InBr₅·H₂O demonstrated a different emission color under additional water exposure, which shows the potential for water detection. The effect of octahedral ligands (H₂O or Cl⁻) on STE emission with different emission wavelengths was investigated.
in Sn-doped Rb InCl₃ and Sn-doped Rb InCl₃ (H₂O) via controlling the distortion of the octahedron. Meantime, the study also suggests that the greater degree of distortion of the octahedron, the more red-shift in STE emission, which provides an effective method to adjust the STE emission color.

Besides all-inorganic In-based perovskites reported, an organic–inorganic In-based [C₆H₄N₂]₂InBr₁₀ single crystal was synthesized via a facile solution-phase method by Kuang’s group. The single crystal [C₆H₄N₂]₂InBr₁₀ demonstrated a broad orange-red PL band from 500 nm to near-infrared region with a long lifetime of 3.2 µs and a large Stokes shift over 300 nm.

Mn-based halide perovskites were also reported. (Pyrrolidinium)MnCl₃ was demonstrated by Xiong’s group, which demonstrated a highly efficient red-light emission under UV excitation as shown in Figure 10h. Strikingly, (Pyrrolidinium)MnCl₃ possesses ferroelectric properties, extending the applications to the field of ferroelectric luminescence or multifunctional devices.

Based on the above discussion, the optical properties and synthesis methods of a large proportion of currently reported lead-free halide perovskite materials are summarized in Table 3.

So far, there are many lead-free halide perovskites reported. It is crucial to understand the structure–property relationship and the underlying mechanisms in terms of reported lead-free halide perovskites. That will provide some effective methods to improve performance. Besides, combining theoretical and experimental approaches to develop new-type lead-free halide perovskites is also very effective.

5. LED Applications

In addition to the considerations of materials, the device designs are also crucial to the development of LED applications. There are two mechanisms for LED light generation: PL and electroluminescence (EL). Correspondingly, lead-free halide perovskite materials are applied to phosphor-converted LEDs and electroluminescent LEDs, as summarized in Tables 4 and 5, respectively.

5.1. Phosphor-Converted LEDs

The phosphor-converted LEDs (pc-LEDs) remain to be a leading position because of their superior luminous efficiency, long operation time, and simple fabrication. The choice of phosphors has a vital influence on the performance of pc-LEDs. As we all know, the rare-earth-based phosphors are the majority in the market, and have made significant advances in pc-LEDs. However, phosphors based on rare-earths also face some problems, such as high cost and recycle difficulty. Low-cost halide perovskites have demonstrated a great promise in pc-LEDs due to their extremely excellent optical properties, including high PLQY, tunable emission, and high color purity. There is a large number of halide perovskites applied to light emission and displays. In order to solve the toxicity issue of lead, developing environmentally benign lead-free perovskite phosphors is necessary.

As shown in Figure 11a, phosphor-converted LEDs are encapsulated by integrating the LED chips and emissive materials, which are widely applied to the fields of lighting and backlight down-converters for liquid crystal displays (LCDs) owing to their superior characteristics. Herein, high energy light sources coming from LED chips (such as InGaN, GaN) are exploited to excite the emissive materials, which can emit lights corresponding to the materials’ optical bandgaps. Obviously, the encapsulants and encapsulation processes affect the performance, duration and stability of the devices.

Several parameters are considered to be significant for depicting the performance of pc-LEDs, including luminous efficacy (LE), color rendering index (CRI), correlated color temperature (CCT) and CIE color coordinates. LE is a measure of how well a light source produces visible light and equals the ratio of luminous flux (lumens, lm) to power (W), which is the foremost specification for pc-LEDs. Generally, LE is used to depict the power consumption of a light source, which is dependent on two factors: the efficiency from electrical power to optical power and the conversion factor from optical power to luminous flux. CRI stands for the ability of a light source to reveal the colors of various objects truly in comparison with an ideal or natural light source. Light sources with a high CRI are desirable in displays and lighting. CCT is the temperature of an ideal black-body radiates light of a color comparable to that of the light source. Generally, the value of CCT over 5000 K is considered as cool white light, and lower CCT is considered as cool white light. CIE color coordinates are quantitative links between wavelengths and human eye perceived colors, usually with the CIE 1931 chromaticity diagram. Besides, CIE 1976 chromaticity diagram was established to solve the uniformity problem of the 1931 chromaticity diagram.

Tang’s group fabricated white light-emitting devices (WLEDs) via a combination of Cs₂Bi₂Br₆ nanocrystal/silica composites and yellow-emitting phosphors under a GaN chip excitation (Figure 11b). The WLEDs demonstrated CIE color coordinates of (0.29, 0.30) and the CCT of 8477.1 K. As shown in Figure 11c, blue-emitting Cs₂SnCl₄:2.75%Bi⁺⁺, yellow-emitting phosphors (Ba₂Sr₂SiO₄:Eu²⁺ and GaAlSiN₃:Eu²⁺) and a 365 nm chip were combined to construct WLEDs, which displayed CIE of (0.36, 0.37) and a warm white with a CCT of 4486 K. The WLEDs with a high color rendering index (CRI ≈ 81) were reported by Li et al., which consisted of orange-emitting Cs₂SnCl₄:0.59%Sr⁺⁺, blue-emitting Cs₂SnCl₄:2.75%Bi⁺⁺ and green-emitting Ba₂Sr₂SiO₄:Eu²⁺ at a ratio of 1:1:1 encapsulated by a silicone polymer with a commercial 380 nm chip.
Table 3. Optical properties and synthesis methods of lead-free halide perovskites (AVC, anti-solvent vapor-assisted crystallization; TLM, temperature lowering method; VHE, vapor halide exchange; VSA, vapor saturation of antisolvent; ASRP, antisolvent reprecipitation method LARP, ligand-assisted reprecipitation method; SEM, slow evaporation method; NCs, nanocrystals; SCs, single crystals; BCs, bulk crystals; TF, thin films; p-FPEA, 4-fluorophenylethylamine; HMD, hexamethylenediamine; TTA, tetraethylammonium; TEBA, benzyltriethylammonium).

| Perovskite           | Abs [nm] | PL [nm] | PLQY [%] | FWHM [nm] | Method          | Refs. |
|----------------------|----------|---------|----------|-----------|----------------|-------|
| 3D CsSnCl₃ NCs       | 588      | 625     | N/A      | 32        | Solvothermal   | [119] |
| 3D CsSnBr₃ NCs       | 622      | N/A     | N/A      | 32        | Solvothermal   | [119] |
| 3D CsSnI₃ NCs        | 668      | 709     | N/A      | 32        | Solvothermal   | [119] |
| 3D CsSnCl₃ NCs       | 420      | 490     | ≤0.14    | N/A       | Hot injection  | [33b] |
| 3D CsSnBr₃ NCs       | 610      | 660     | ≤0.14    | N/A       | Hot injection  | [33b] |
| 3D CsSnI₃ NCs        | 750      | 945     | ≤0.14    | N/A       | Hot injection  | [33b] |
| 3D Cs₂SnI₆ NCs       | N/A      | 620     | ≤0.48    | 49        | Hot injection  | [66a] |
| 3D Cs₂SnCl₆:Bi³⁺ BCs | N/A      | 455     | 78.9     | 66        | Hydrothermal   | [16e] |
| 3D Cs₂SnCl₆:Sb³⁺ BCs | N/A      | 602     | 37       | 101       | Hydrothermal   | [187] |
| 3D p-FPEA₃Sn₄ NCs    | 621.2    | 640     | 9.94 ± 1.23 | 30.8 | ASRP          | [44]  |
| 2D (OCTAm)₂SnI₄ BCs  | 350      | 600     | 95 ± 5   | 136       | Solution process | [56] |
| 2D (OAm)₂SnBr₂ BCs   | N/A      | 620     | 88       | 140       | Hot injection  | [86]  |
| 2D (PEAl)₃(Csl₄) NCs | N/A      | 920     | 18       | N/A       | Spin-coating   | [188] |
| 2D (C₆H₅NH₃)₂SnBr₂ BCs | N/A | 596     | 98       | N/A       | Solution process | [189] |
| 2D (OAm)SnI₄ SCs     | N/A      | 634     | 20.3     | 142       | Solution process | [35]  |
| 2D (OAm)SnI₄ TFs     | N/A      | –       | 36       | 145       | Solution process | [35]  |
| 0D (C₆H₆H₅Br₃)SnBr₅ SCs | 355 | 570   | 95 ± 5   | 105       | Solution process | [312] |
| 0D (C₆H₆H₅I₅)SnI₅ SCs | 410 | 620 | 75 ± 4  | 118       | Solution process | [312] |
| 0D Cs₂SnBr₃ powder   | N/A      | 540     | 15 ± 5   | N/A       | Solid-state process | [153] |
| 0D Cs₂SnBr₃ BCs      | 320      | 524     | 20       | 100       | ASRP          | [190] |
| 0D Cs₂KSnBr₃ BCs     | 320      | 500     | 35       | 100       | ASRP          | [190] |
| 0D Cs₂SnBr₃ NCs      | N/A      | 530     | 0.8      | 45        | Hot injection  | [191] |
| 0D Bmpip₂SnBr₃ SCs   | N/A      | 666     | 75       | N/A       | TLM           | [134] |
| 0D Bmpip₂SnI₄ SCs    | N/A      | 730     | 35       | N/A       | TLM           | [134] |
| 0D HMD₃SnBr₅ BCs     | N/A      | 601     | 86 ± 2   | 128       | Antisolvent method | [192] |
| 2D (C₆H₆H₅NH₃)₃GeI₃ SCs | 690 | N/A  | 180      | Solution process | [137] |
| 2D (PEAl)₃Ge₅ BCs   | N/A      | 613     | N/A      | 98.4      | Solution process | [138] |
| 0D Bmpip₂GeBr₃ SCs   | N/A      | 670     | ≤1       | N/A       | Solution process | [134] |
| 2D MA₂Bi₃ Br₅ SCs    | N/A      | 550     | N/A      | 100       | SEM           | [143] |
| 2D MA₂BiCl₃ NCs      | N/A      | 360     | 15       | 50        | Co-LARP       | [143] |
| 2D MA₂Bi₅ Br₅ NCs    | 376      | 423     | 12       | 62        | Co-LARP       | [143] |
| 2D MA₂Bi₅ I₅ NCs     | N/A      | 540     | 0.03     | 91        | Co-LARP       | [143] |
| 2D MA₂Bi₅ Br₅–Cl NCs | 388      | 422     | 54.1     | N/A       | Co-LARP       | [144] |
| 2D Cs₂Bi₂ Br₅ NCs    | N/A      | 460     | 4.5      | 45        | Co-LARP       | [58]  |
| 2D Cs₂Bi₂ Cl₅ NCs    | N/A      | 393     | 26.4     | 59        | Co-LARP       | [58]  |
| 2D Cs₂Bi₂ Br₅ NCs    | N/A      | 410     | 19.4     | 48        | Co-LARP       | [58]  |
| 2D Cs₂Bi₂ I₅ NCs     | N/A      | 545     | 0.018    | 70        | Co-LARP       | [58]  |
| 2D Fa₂Bi₂ Br₅ NCs    | 404      | 437     | 52       | 65        | Co-LARP       | [193] |
| 0D Rb₂Bi₂Cl₄ NCs     | N/A      | 437     | 28.43    | 93        | LARP          | [79]  |
| 0D (C₆H₆H₅)₂Br₃•H₂O SCs | 400 | 450 | 0.7   | N/A       | TLM          | [78]  |
| 0D (C₆H₆H₅NH₃)₂Br₃•H₂O SCs | N/A | 400–850 | 4.5 | N/A       | TLM          | [78]  |
| 0D (C₆H₆H₅)₂SbCl₄ SCs | N/A | 590 | 98 ± 2 | 119       | Solution process | [132] |
| 0D (Ph₄P)₂SbCl₄ SCs  | N/A      | 648     | 87 ± 2   | 136       | AVC           | [82]  |

(Continued)
Table 3. Continued.

| Perovskite | Abs [nm] | PL [nm] | PLQY [%] | FWHM [nm] | Method | Refs. |
|------------|----------|--------|----------|-----------|--------|-------|
| 0D (TTA)$_2$SbCl$_5$ powder | N/A | 625 | 86 | 140 | ASRP | [194] |
| 0D (TEBA)$_2$SbCl$_5$ powder | N/A | 590 | 98 | 135 | ASRP | [194] |
| 2D Cs$_2$Sb$_2$Cl$_6$ NCs | N/A | 370 | 11 | 52 | LARP | [80] |
| 2D Cs$_2$Sb$_2$Br$_5$ NCs | N/A | 410 | 46 | 41 | LARP | [80] |
| 2D Cs$_2$Sb$_2$I$_6$ NCs | N/A | 560 | 23 | 56 | LARP | [80] |
| 2D Cs$_2$Sb$_2$I$_6$ TFs | N/A | 750 | N/A | 120 | VHE | [156] |
| 2D Cs$_2$Sb$_2$Br$_5$ NCs | 368 | 409 | 51.2 | N/A | ASRP | [66b] |
| 2D (NH$_4$)$_3$Sb$_2$I$_9$ TFs | 645 | 639 | N/A | N/A | AVC | [155] |
| 3D Cs$_2$AgBiCl$_6$ NCs | N/A | 395 | 6.7 | 68 | LARP | [62] |
| 3D Cs$_2$AgBiBr$_6$ NCs | N/A | 465 | 0.7 | 82 | LARP | [62] |
| 3D Cs$_2$AgBiI$_6$ NCs | N/A | 575 | <0.1 | 69 | LARP | [62] |
| 3D Cs$_2$AgBiCl$_6$:Mn$^{2+}$ NCs | N/A | 600 | <1 | N/A | Solution process | [163] |
| 3D Cs$_2$AgInCl$_6$:Ag$^{3+}$ NCs | 368 | 395/570 | 36.6 | N/A | ASRP | [24] |
| 3D Cs$_2$AgInCl$_6$:Mn$^{2+}$ NCs | 350 | 620 | ≈16 ± 4 | N/A | Hot injection | [167] |
| 3D Cs$_2$AgInCl$_6$:Bi$^{3+}$/Yb$^{3+}$/Er$^{3+}$ NCs | N/A | 557 | 64 | 153 | ASRP | [168] |
| 3D Cs$_2$AgInCl$_6$:Bi$^{3+}$/Mn$^{2+}$/BCs | N/A | 605 | 86 ± 5 | N/A | Hydrothermal | [60] |
| 3D Cs$_2$AgInCl$_6$:Bi$^{3+}$/Mn$^{2+}$/BCs | 368 | 580 | 3.5 | N/A | Solution process | [163] |
| 3D Cs$_2$CuBr$_4$ NCs | 360 | 393 | 37.5 | 74 | LARP | [179] |
| 3D Cs$_2$CuBr$_4$ NCs | N/A | 388 | 51.82 | 68 | LARP | [179] |
| 3D Cs$_2$CuBr$_4$ NCs | N/A | 495 | N/A | 70 | Solution process | [168] |
| 1D Cs$_2$CuI$_3$ NRs | 330 | 553 | 5 | N/A | Hot injection | [177] |
| 0D Cs$_2$CuI$_3$ NCs | 285 | 441 | 67 | N/A | Hot injection | [177] |
| 0D Cs$_2$CuI$_3$ NCs | 277 | 454 | 18.3 | 82 | Hot injection | [177] |
| 1D Cs$_2$CuI$_3$ powder | N/A | 527 | 48 | 102 | Solid-state reaction | [200] |
| 1D Cs$_2$CuI$_3$ powder | N/A | 533 | 18.3 | 106 | Solid-state reaction | [200] |
| 1D Cs$_2$CuI$_3$ powder | N/A | 576 | 3.23 | 126 | Solid-state reaction | [200] |
| 0D Cs$_2$CuI$_3$ powder | N/A | 455 | 50.1 | 75 | Solid-state reaction | [176] |
| 0D Cs$_2$CuI$_3$ powder | N/A | 443 | 98.7 | 99 | Solid-state reaction | [176] |
| 0D Cs$_2$CuI$_3$ NCs | N/A | 445 | 91.2 | N/A | VSA | [61] |
| 0D Cs$_2$CuI$_3$ TFs | N/A | 445 | 62.1 | N/A | Spin-coating | [61] |
| 0D Cs$_2$CuI$_3$ NCs | 285 | 445 | 29.2 | N/A | Hot injection | [201] |
| 0D Cs$_2$CuI$_3$ NCs | 269 | 461 | 16.9 | N/A | Hot injection | [201] |
| 0D Cs$_2$CuI$_3$ NCs | 259 | 527 | 48.7 | N/A | Hot injection | [201] |
| 1D Cs$_2$CuI$_3$ TFs | N/A | 550 | 20.6 | 100 | Antisolvent method | [213] |
| 1D Cs$_2$CuI$_3$ SCs | N/A | 568 | 15.7 | 75 | Antisolvent method | [202] |
| 0D Cs$_2$InBr$_3$·H$_2$O SCs | N/A | 695 | 33 | N/A | TLM | [72] |
| 0D Rb$_2$InCl$_6$(H$_2$O):Sb$^{3+}$ SCs | 324 | 600 | 90 | N/A | Hydrothermal | [182] |
| 0D Rb$_2$InCl$_6$:Sb$^{3+}$ SCs | N/A | 497 | 95 | N/A | Solvent thermal | [182] |
| 0D (C$_2$H$_4$N$_2$)$_3$In$_3$:Br$_9$ SCs | 335 | 670 | 3 | N/A | Solution process | [183] |
| 3D Cs$_2$Yb$_3$:NCs | N/A | 671 | 58 | 47 | Hot injection | [180] |
| 3D Cs$_2$TiBr$_4$ TFs | N/A | 704 | N/A | N/A | Vapor deposition | [97] |
| 3D Cs$_2$PdBr$_3$ SCs | 784 | 772 | N/A | N/A | Solution process | [179] |
| 1D (Pyrrolidinium)MnCl$_3$ SCs | N/A | 637 | 56 | N/A | SEM | [185] |
Table 4. Phosphor-converted LEDs from lead-free halide perovskites.

| Emitting material | Device structure | CCT [K] | CIE coordinates | CRI | Stability |
|-------------------|-----------------|---------|-----------------|-----|-----------|
| Cs₂SnCl₆:2.75%Bi³⁺ | Cs₂SnCl₆:2.75%Bi³⁺ / Ba₅Sr₃SiO₈:Eu²⁺ / Ga₅Si₅N₄:Eu²⁺ (silicone) | 4486 | (0.36, 0.37) | N/A | N/A |
| Cs₂Ag₀.₆Na₀.₄InCl₆:0.04Bi³⁺ | Cs₂Ag₀.₆Na₀.₄InCl₆:0.04Bi³⁺ / ultravioletchip | 6815 | (0.30, 0.37) | 81 | N/A |
| (OCTAm)₂SnBr₄ | (OCTAm)₂SnBr₄ / Ba₅Mg₅Al₁₀O₁₇:Eu²⁺ / G₂₇₆ / 365 nm chip (TEOS) | 6815 | (0.30, 0.37) | 81 | N/A |
| Cs₃Bi₂Br₉ | Cs₃Bi₂Br₉ / Cs₂SnCl₆:2.75%Bi³⁺ / Ba₅Sr₃SiO₈:Eu²⁺ / 380 nm chip (TEOS) | 6815 | (0.30, 0.37) | 81 | N/A |

Table 5. Electroluminescent LEDs from lead-free halide perovskites.

| Emitting material (EM) | Device structure | EL [nm] | EQE max [%] | CE max [cd Å⁻¹] | L max [cd m⁻²] |
|------------------------|-----------------|---------|-------------|-----------------|----------------|
| CsSnI₃ | ITO/PEDOT/PBD/LiF/Al | 950 | 3.8 | N/A | N/A |
| MASn(Br₀.₅I₀.₅)₃ | ITO/PEDOT:PSS/EM/F8/Ca/Ag | 667 | 0.007 | N/A | N/A |
| MASn(Br₀.₄I₀.₆)₃ | ITO/PEDOT:PSS/EM/F8/Ca/Ag | 825 | 0.046 | N/A | N/A |
| MASn(Br₀.₃I₀.₇)₃ | ITO/PEDOT:PSS/EM/F8/Ca/Ag | 868 | 0.058 | N/A | N/A |
| MASn(Br₀.₂I₀.₈)₃ | ITO/PEDOT:PSS/EM/F8/Ca/Ag | 896 | 0.11 | N/A | N/A |
| MASnI₃ | ITO/PEDOT:PSS/EM/F8/Ca/Ag | 945 | 0.72 | N/A | N/A |
| PEA₂SnI₄ | ITO/PEDOT:PSS/EM/F8/LiF/Al | 618 | N/A | 0.029 | 0.15 |
| TEA₂SnI₄ | ITO/PEDOT:PSS/EM/TBPB/LiF/Al | 633 | 0.3 | N/A | 70 |
| (OAm)₂SnBr₄ | ITO/PEDOT/PSS/EM/TBPB/LiF/Al | 638 | 0.62 | N/A | 322 |
| (PEAI)₃(CsI)₅(SnI₂)₄ | ITO/PEDOT/PSS/EM/TBPB/LiF/Al | 625 | 0.1 | 0.029 | 350 |
| Cs₂Ag₀.₆Na₀.₄InCl₆:0.04Bi³⁺ | PEIE-IITO/PEIE-ZnO/EM/TAPC/MoOₓ/LiF/Al | N/A | 0.11 | N/A | 60 |
| CsCuBr₃ | Ag/EM/p-Si-In Ga | 527 | N/A | N/A | N/A |
| Cs₃Cu₂I₅ | Ag/ZSO/EM/NPD/MoOₓ/Ag | 440 | N/A | N/A | 10 |
| Cs₂CuI₃ | ITO/PEDOT/PSS/Poly-TPD/EM/TBPB/LiF/Al | 550 | 0.17 | 0.46 | 47.5 |
| Cs₂CuI₃ | Glass/IITO/PEDOT/PSS/EM/TBPB/LiF/Al | 445 | 1.12 | N/A | 263.2 |
| Cs₂SbBr₃ | Glass/IITO/PEDOT/PSS/EM/TBPB/LiF/Al | N/A | 10⁻⁸ | N/A | 190 |
| Cs₂SbBr₃ | Glass/IITO/PEDOT/PSS/EM/TBPB/LiF/Al | 408 | ~0.206 | N/A | 660 |
| CsSnBr₃ | Glass/IITO/EM/LiF/ZnS/Ag | 672 | 0.34 | N/A | N/A |

operation currents, which might be attributed to no energy transfer between the two phosphors. Blue-emitting Cs₃Cu₂I₅ with a yellow-emitting phosphor were mixed into a polydimethylsiloxane matrix, which demonstrated bright white emission under UV illumination (Figure 11b).  

5.2. Electroluminescent LEDs

Electroluminescent devices can emit light when the injected electrons and holes encounter and radiatively recombine in the active layer. In fact, solution-processed lead-based halide perovskites have been widely investigated in electroluminescent LEDs with a considerable progress. The EQE of lead-based halide perovskite LEDs have been rapidly improved from the initial 0.76% to over 20% in recent years. So far, the maximum EQE of perovskite LEDs for green, red and infrared emission have reached 28.2%, 21.3%, 21.6%, respectively. As for the blue-emitting LEDs, the maximum EQE has also reached 9.5%. A typical electroluminescent device structure is demonstrated in Figure 12a. The structure consists of an anode, a hole transport layer...
Figure 11. a) Schematic of phosphor-converted LED. b) EL spectrum of the WLED by integrating blue-emitting Cs$_2$Bi$_2$Br$_3$ NCs and yellow-emitting rare-earth phosphor Y$_3$Al$_5$O$_{12}$. Inset: device photos of NCs/silica composites combined with Y$_3$Al$_5$O$_{12}$ (off and on). Reproduced with permission.[35] Copyright 2017, Wiley-VCH. c) CIE color coordinates of WLED device combined by Cs$_2$SnCl$_6$:2.75%Bi$_3^+$/Ba$_2$Sr$_2$SiO$_4$:Eu$_2^+$/GaAlSiN$_3$:Eu$_2^+$/365 chip and inset image of operating LED. Reproduced with permission.[16e] Copyright 2018, Wiley-VCH. d) 365 nm UV pumped single yellow-emitting (OCTAm)$_2$SnBr$_4$ LED and WLED fabricated by (OCTAm)$_2$SnBr$_4$/BaMgAl$_{10}$O$_{12}$:Eu$_2^+$/G2762/365 nm UV chip. Reproduced with permission.[58] Copyright 2019, Royal Society of Chemistry. e) XRD patterns of a Cs$_2$Ag$_{0.6}$Na$_{0.4}$InCl$_6$ films (top) and powder (bottom). The inset displays a 300 nm thick quartz substrate and 500 nm thick Cs$_2$Ag$_{0.6}$Na$_{0.4}$InCl$_6$ films under the excitation of 254 nm. f) Operational stability of Cs$_2$Ag$_{0.6}$Na$_{0.4}$InCl$_6$ devices, measured in air without any encapsulation. Reproduced with permission.[40] Copyright 2018, Springer Nature. g) EL spectra of a WLED at different driving currents, the insets show the device when off and on. Reproduced with permission.[132] Copyright 2018, Royal Society of Chemistry. h) Photograph of Cs$_3$Cu$_2$I$_5$, a yellow phosphor, and its mixtures (from left to right: Cs$_3$Cu$_2$I$_5$, mixture of 2:8, yellow phosphor) under UV excitation (top) and films prepared by kneading the powders into polydimethylsiloxane matrix (bottom). Reproduced with permission.[61] Copyright 2018, Wiley-VCH.

Figure 12. a) Schematic representation of typical electroluminescent device structure. Reproduced with permission.[22] Copyright 2016, Springer Nature. b) Normalized EL spectra of ITO/PEDOT:PSS/CH$_3$NH$_3$Sn(Br$_{1-x}$I$_x$)$_3$/F8/Ca/Ag LED. Reproduced with permission.[206] Copyright 2016, American Chemical Society. c) Dependence of the current density and radiance on the driving voltage for (PEAI)$_x$(CsI)$_y$(SnI$_2$)$_z$. d) EQE values versus current density for (PEAI)$_x$(CsI)$_y$(SnI$_2$)$_z$. For the (PEAI)$_x$(CsI)$_y$(SnI$_2$)$_{4.5}$ MQW-based LED, a maximum EQE of 3% is achieved. Reproduced with permission.[188] Copyright 2017, American Chemical Society. e) Cross-sectional picture of the ITO/PEDOT:PSS/Cs$_3$Sb$_2$I$_9$ thin film/TPBi/LiF/Al device. Reproduced with permission.[156] Copyright 2019, American Chemical Society. g) PL spectrum of the CsCuBr$_2$ micro-crosses on the Si substrate and EL spectrum of the LED at 2.8 V. Inset: a PL photograph of the CsCuBr$_2$ micro-crosses. Reproduced with permission.[198] Copyright 2019, Royal Society of Chemistry. h) Simplified energy levels of each layer of the heterostructure in LED based on Cs$_3$Sb$_2$Br$_9$ nanocrystals. Reproduced with permission.[195] Copyright 2019, American Chemical Society.
(HTL), an emitter layer, an electron transport layer (ETL) and a cathode. Under an applied voltage, the electrons and holes can be injected from cathode and anode through ETL and HTL to emitter layer to form excitons and subsequently emit light.[211] There are two significant specifications related to LED performance: PLQY and EL intensity. The PLQY of the emitter layer is widely used to describe the optoelectronic quality of the emitter layer.[212] However, consideration for PLQY of the active layer alone is not sufficient to achieve good performance. The internal quantum efficiency (IQE) is defined as the proportion between the number of photons emitted in the emitter layers and the number of electrons injected into the LED. To obtain a larger IQE, the non-radiative electron–hole recombination should be minimized and charges should not pass through the device in the absence of radiative recombination. Hence, the electron and hole blocking layers should be applied. The transport layers also serve as blocking layers to keep electrons and holes from escaping from the emissive layer.[213] Moreover, there is a relationship $\eta = \eta_0 \cdot \text{IQE}$, where $\eta_0$ is an optical outcoupling coefficient, describing as how many emitted photons can be extracted from the LED into the free space or the fraction of emitted photons that are coupled out of the device. The higher IQE values of electroluminescent LEDs are actively pursued.

In addition, the figures of merit that evaluate the performance of LEDs also include current efficiency (CE), maximum luminance ($L_{\text{max}}$), turn-on voltage ($V_{\text{on}}$), and operational stability. CE is $L/IJ$, where $L$ and $J$ are the luminance of the LED and the current density, respectively, and $V_{\text{on}}$ is defined as the required voltage to make the luminance of 1 cd m$^{-2}$. These parameters are crucial to evaluate the performance of the electroluminescent LEDs.[214]

The carrier mobility must be emphasized in electroluminescent LEDs. The mobility is the speed that a charge carrier moves through a conductor in the presence of an electric field. The mobility of carriers and exciton binding energy are two important parameters for optoelectronic devices, which can influence the carrier recombination process. The efficient carrier injection and radiative recombination are in demand, whereas the nonradiative recombination originating from defects and Auger recombination should be avoided. The larger exciton binding energy and moderate mobility are beneficial for improving the radiative recombination. Low mobility can lead to electron aggregation at one side of the devices and hole aggregation at the other side, which will aggravate the Auger recombination. There is an exceptional review relevant to engineering charge transport in heterostructured materials.[21]

So far, there are only a few reports on lead-free halide perovskites for electroluminescent LED applications. Among them, infrared electroluminescent LEDs account for the majority. Early in 2016, Tan’s group reported a series of electroluminescent LEDs based on CH$_3$NH$_3$SnBr$_x$I$_{3-x}$ (x = 0.5–1) thin films with the device structure of ITO/PEDOT:PSS/CH$_3$NH$_3$SnBr$_x$I$_{3-x}$/F8/Ca/Ag. As shown in Figure 12b, the EL peak ranged from 667 to 945 nm under different Br/I ratios, and a maximum EQE of 0.72% was obtained when the emissive material was CH$_3$NH$_3$SnI$_3$ thin films.[206] As is known to all, high-quality thin films are favorable for the LED performance. Chao’s team reported that the infrared LEDs fabricated by high-quality CsSnI$_3$ thin films exhibited outstanding properties. The device structure was ITO/PEDOT:PSS/CsSnI$_3$ thin films/F8/LiF/Al. The EL peak located at 950 nm with a maximum radiance of 40 W sr$^{-1}$ m$^{-2}$ and a maximum EQE of 3.8% was obtained.[209]

Quasi-2D perovskites with multiple quantum-well structures showed good stability, high PLQY and excellent performance in LEDs. The high PLQY can be ascribed to cascade energy transfer and exciton confinement.[217] Expectably, Sn-based 2D perovskites were exploited to fabricate electroluminescent LEDs for the first time and exhibited good results. The synthesized (PEAI)$_x$(CsI)$_y$(SnI$_3$)$_z$ uniform and stable thin films showed a series of EL spectra by adjusting the precursor ratio. The highest EQE of up to 3% at 920 nm with a radiance of 40 W sr$^{-1}$ m$^{-2}$ was achieved by (PEAI)$_x$(CsI)$_y$(SnI$_3$)$_z$ as shown in Figure 12c,d.

In addition to infrared electroluminescent LEDs, visible electroluminescent LEDs based on 2D Sn-based perovskites were also studied by Zhang’s and Haque’s groups.[86,129] A bright orange-emitting electroluminescent LED using (OAm)$_2$SnBr$_4$ with a device structure of ITO/PEI-ZnO/perovskite/TCTA/MoO$_3$/Au was fabricated. A maximum luminance of 350 cd m$^{-2}$ was obtained, which is the highest brightness in lead-free electroluminescent LEDs. A red LED with structure of ITO/PEDOT:PSS/(PEA)$_2$SnI$_4$/F8/LiF/Al (PEDOT:PSS and F8 were hole and electron injection layers, respectively) (Figure 12e) showed an EL peak at 618 nm with a current efficacy (CE) of 0.003 cd A$^{-1}$ and luminance up to 0.15 cd m$^{-2}$.[219] The pure red-emitting Sn-based electroluminescent LEDs were reported and displayed the improved performance.[143] When TEA$_2$SnI$_4$ served as the emission layer in the ITO/PEDOT:PSS/emission layer/TPBi/LiF/Al device, the electroluminescent LEDs demonstrated a low turn-on voltage of 2.3 V, a maximum EQE of 0.62% and maximum luminance of 322 cd m$^{-2}$.[207] For the 2D perovskites applied to optoelectronic devices, the charge transport between the inorganic layers is limited due to the block of organic layers. To overcome this issue, a vertical crystal arrangement was adopted in the optoelectronic devices, which means that the inorganic layers are perpendicular to the substrate and facilitate the efficient charge carrier transport.[126]

Sb-based perovskite thin films were first introduced in the electroluminescent LEDs by Chu’s group, and the device structure was ITO/PEDOT:PSS/CsSbI$_3$ thin film/TPBi/LiF/Al. Figure 12f demonstrates the rapid increase of current density under the condition of 2 V voltage, and the radiance of 0.012 W sr$^{-1}$ m$^{-2}$ at 6 V.[156] Yuan et al. fabricated a series of CsSnX$_3$ thin films and utilized them to fabricate a red-emitting electroluminescent LED, which had a current density as high as 915 A cm$^{-2}$.[101] In addition to the red-emitting electroluminescent LEDs, green- and blue-emitting electroluminescent LEDs were also reported using lead-free perovskites. A green EL at 527 nm was observed via integrating Cs$_2$CuBr$_4$ micro-crosses (MCs) in the device structure of Ag/Cs$_2$CuBr$_4$/p-Si/In–Ga, as shown in Figure 12g. The peak shift between PL and EL was attributed to the different emission mechanisms.[198] The PL originates from Cs$_2$CuBr$_4$ surface, whereas the EL is generated at the Cs$_2$CuBr$_4$ MC/p-Si interface due to the recombination of electrons and holes. Hosono’s group showed a blue electroluminescent LED based on Cs$_2$CuI$_3$ thin films, and the maximum luminance was approximately 10 cd m$^{-2}$.[61] Tang’s group also reported an electroluminescent LED based on Cs$_2$Ag$_{0.8}$Na$_{0.4}$InCl$_3$·Bi$^{3+}$ and demonstrated a low efficiency. Above-mentioned electroluminescent LEDs based on
Cs$_2$Cu$_3$I$_x$ and Cs$_2$Ag$_{0.5}$Na$_{0.5}$InCl$_6$:Bi$^{1+}$ were originated from STE emission. The low EQEs are due to the low carrier mobility owing to low electronic dimensionality, strong coupling to the lattice, and the poor charge injection because of the material's large band gap.\[109a\]

Electroluminescent LEDs using lead-free halide perovskite nanocrystals were first reported by Shi’s group. As shown in Figure 12h, the suitable energy level structures were exploited, where TCTA served as the hole-transporting layer and electron blocking layer owing to the suitable VBM and electron affinity. Electroluminescent LEDs using Cs$_2$Sb$_2$Br$_9$ quantum dots manifested a violet emission at 408 nm and with an EQE of $\approx$0.206%.\[66\] There are reasons that these lead-free perovskite nanocrystal electroluminescent LEDs are rare. On the one hand, it is due to the inferior characteristics of lead-free perovskite nanocrystals including low PLQY, wide FWHM, and poor stability.\[218\] On the other hand, the key obstacles of performance for nanocrystal film-based devices were the presence of organic ligands and nonuniform films. The surface organic ligands serving as an insulating layer block charge injection into the emitter in LEDs. Besides, films of nanocrystals typically consist of agglomerates and clusters, which technically can be improved by using a nanocrystal solution with low concentration. Moreover, common surface ligand oleic acid and oleylamine, weakly bonded to nanocrystals, would degrade under device operating conditions.\[219\] Hence, choosing proper ligands to improve the device’s performance is significant, which has been reported in lead-based halide perovskite devices.\[220\] In addition, the nanocrystal film quality can be improved via interface engineering, such as a simple posttreatment utilizing PEI (polyethyleneimine), which has been proven to be effective in obtaining high-quality perovskite nanocrystal thin-films.\[210\]

### 6. Summary and Outlook

The lead-free halide perovskite materials have drawn increasing attention due to the environmentally benign property in optoelectronic applications. In recent years, enormous efforts have been devoted to exploiting lead-free halide perovskites. A large number of low-toxic or nontoxic metal cations such as Sn (II), Sn (IV), Ge (II), Bi (III), Sb (III), Ag (I), Cu (II), and Cu (I), have replaced Pb (II). In this review, we highlighted the excellent characteristics of halide perovskites that benefit light generation, including the defect-tolerance, bandgap type, and exciton binding energy. We summarized the synthesis methods of lead-free halide perovskites, and systematically reviewed the optoelectronic properties of reported lead-free halide perovskites, specially at different molecular dimensionalities with various forms of single crystals, thin films and nanocrystals. The LED applications of lead-free halide perovskite were also delved.

However, there are still many issues to be solved in future research. Searching for lead-free halide perovskites with high performance is still urgent and necessary. For the most reported lead-free halide perovskites, the FWHM of emission is wider than lead halide perovskites, which is not suitable for display applications. More efforts should be made to develop lead-free halide perovskites with narrow-band emission for ultrahigh definition displays. The emissions of lead-free halide perovskites originated from STEs have an excellent promise in WLED applications.\[60\] In addition, we believe that lead-free Sn-based halide perovskites also demonstrate vast potential in near-infrared emissions, which can be widely applied to plant growth, bioimaging, optical data communication, and night-vision devices.

The performance of LEDs using lead-free halide perovskite materials is far from those with lead halide perovskites. More efforts are needed to make significant advances in material preparations and device engineering on film/interlayer optimizations. The theoretical and computational material screening has been widely applied in the solar cells, which will give us some guidance to develop new lead-free halide perovskites for other optoelectronic applications.\[222\] As we all know, the first-principles high-throughput computational material screening is a useful tool to accelerate material discovery. Yang’s group identified 23 organic–inorganic hybrid halide semiconductor candidates for light-emitting materials through high-throughput calculations.\[140\] Recently, Zhang’s group summarized the different screening criteria for the materials applied to various optoelectronic applications, including photovoltaic solar cells, photoelectrochemical cells, and LEDs.\[222\] These selected materials can be synthesized via the proper methods. The investigations combined with theoretical, computational, and experimental methods will tremendously promote the development of lead-free perovskite materials.\[224\]

For the phosphor-converted LEDs, warm WLED lighting devices with long lifetimes are in demand. Hence, it is significant to develop the lead-free halide perovskites with suitable excitation wavelengths and proper device encapsulation. For the electroluminescent LEDs, the lead-free halide perovskites or lead-free halide materials with high PLQY do not guarantee good LED performance. Exploiting lead-free halide perovskites with high PLQY and excellent carrier mobilities is a final goal. Besides, the quality of lead-free halide perovskite thin films cannot be ignored. Doping and post-treatment are two significant strategies to improve perovskite thin film quality, which have been proven to be extremely effective in the field of perovskite solar cells.\[24,225\] The reported emissive layers consist mainly of low-dimensional perovskites or low-dimensional Cu-based halide materials, including 0D Cs$_2$Cu$_3$I$_5$, 1D Cs$_2$Cu$_3$I$_4$, 2D Cs$_2$Sb$_2$Br$_9$, 2D (OAm)$_2$SnBr$_4$, 2D PEA$_2$SnI$_4$, 2D TEA$_2$SnI$_4$, 2D (PEAI)$_2$[(CsI)$_3$(SnI)$_4$].\[66,86,136,195,206,208,228\] Low-dimensional perovskites or halide materials generally possess low electronic dimensionalities and result in low carrier mobilities and undesirable performances. Besides, the large organic group in low-dimensional perovskites also impede the carriers transport. Moreover, for lead-free halide perovskites with large bandgap or high energy emission, the poor charge injection originated from the energy-level mismatch is a critical reason for insufficient EL characteristics. The charge injection balance needs appropriate energy band alignment and proper mobility. The energy barrier between the charge transport layers and perovskites directly determines the charge injection efficiency of LEDs. Therefore, it is crucial to choose the suitable ETLs and HTLs. We believe that exploiting multifunctional charge transporting layer (CTL) materials is also vital, wherein the CTLs can improve the charge transport and influence the heterointerfaces. Excellent multifunctional CTLs may have some active influences, such as phase control, defect passivation, ion migration reduction, and light outcoupling modulation. Some effective methods of improving...
E QE have been explored, which can give us some inspiration to develop LEDs based on perovskites and these methods have obtain superior results in OLEDs and QLEDs. [226] For instance, out-coupling is regarded as an efficient strategy to maximize the EQE in OLEDs and GaN LEDs. Technically, exploiting the localized surface plasmon resonance and enhancing photon extraction via a half-ball lens and other ways have been confirmed to be effective in perovskite LEDs. [12a,227] In addition to the LEDs, light-emitting electrochemical cells (LECs) also show great promise as electroluminescent devices for display and lighting. Compared with LEDs, LECs are considered the simplest thin-film lighting devices to date. Hence, developing LECs based on lead-free halide perovskites for displays and lighting also deserves attention. To fulfill the standard of Rec.2020 defined the display color gamut, and achieve ultrahigh definition displays, laser displays based on halide perovskites are considered to be a crucial technology for the development of next-generation display. [116a]

In the future, laser displays based on lead-free halide perovskites are promising, requiring more attention in both materials and technology. In conclusion, developing lead-free halide perovskites and fabricating lead-free halide perovskite LEDs with outstanding properties are urgent and necessary but challenging, which requires more efforts.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

lead-free perovskites, LEDs, light emission, nanomaterials

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[1] a) A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, J. Am. Chem. Soc. 2009, 131, 6050; b) Best Research-Cell Efficiency Chart, https://www.nrel.gov/pv/cell-efficiency.html; accessed (August, 2020).

[2] a) Y. Gao, Y. Wu, H. Lu, C. Chen, Y. Liu, X. Bai, L. Yang, W. W. Yu, Q. Dai, Y. Zhang, Nano Energy 2019, 59, 517; b) W.-J. Yin, T. Shi, Y.-Y. Gao, Adv. Mater. 2014, 26, 4653; c) A. Miyata, A. Mitiglu, P. Plachocka, O. Portugall, J.-T. W. Wang, S. D. Stranks, H. J. Snaith, R. J. Nicholas, Nat. Phys. 2015, 11, 582; d) H.-S. Duan, H. Zhou, Q. Chen, P. Sun, S. Luo, T.-B. Song, B. Bob, Y. Yang, Phys. Chem. Chem. Phys. 2015, 17, 112; e) C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith, L. M. Herz, Adv. Mater. 2014, 26, 1584; f) O. Voznyy, B. R. Sutherland, A. H. Ip, D. Zhitomirsky, E. H. Sargent, Nat. Rev. Mater. 2017, 2, 17026.
[223] S. Luo, T. Li, X. Wang, M. Faizan, L. Zhang, WIREs Comput. Mol. Sci. 2020, e1489, https://doi.org/10.1002/wcms.1489.

[224] B. Vargas, R. Torres-Cadena, D. T. Reyes-Castillo, J. Rodríguez-Hernández, M. Gembicky, E. Menéndez-Prupin, D. Solís-Ibarra, Chem. Mater. 2020, 32, 424.

[225] Y. Gao, Y. Wu, Y. Liu, C. Chen, X. Bai, L. Yang, Z. Shi, W. W. Yu, Q. Dai, Y. Zhang, ACS Appl. Mater. Interfaces 2020, 12, 3631.

[226] a) M. A. Fusella, R. Saramak, R. Bushati, V. M. Menon, M. S. Weaver, N. J. Thompson, J. J. Brown, Nature 2020, 585, 379; b) S. Wang, X. Dou, L. Chen, Y. Fang, A. Wang, H. Shen, Z. Du, Nanoscale 2018, 10, 11651.

[227] X. Zhang, B. Xu, W. Wang, S. Liu, Y. Zheng, S. Chen, K. Wang, X. W. Sun, ACS Appl. Mater. Interfaces 2017, 9, 4926.

[228] Z. Ma, Z. Shi, C. Qin, M. Cui, D. Yang, X. Wang, L. Wang, X. Ji, X. Chen, J. Sun, D. Wu, Y. Zhang, X. Li, L. Zhang, C. Shan, ACS Nano 2020, 14, (4), 4475.

[229] W.-L. Hong, Y.-C. Huang, C.-Y. Chang, Z.-C. Zhang, H.-R. Tsai, N.-Y. Chang, Y.-C. Chao, Efficient Low-Temperature Solution-Processed Lead-Free Perovskite Infrared Light-Emitting Diodes Advanced Materials 2016, 28, (36), 8029. https://doi.org/10.1002/adma.201601024.

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