Low-Dimensional Metal Halide Perovskite Crystal Materials: Structure Strategies and Luminescence Applications

Ying Han, Sijia Yue, and Bin-Bin Cui*

Replacing methylammonium (MA⁺), formamidine (FA⁺), and/or cesium (Cs⁺) in 3D metal halide perovskites by larger organic cations have built a series of low-dimensional metal halide perovskites (LDMHPs) in which the inorganic metal halide octahedra arranging in the forms of 2D layers, 1D chains, and 0D points. These LDMHPs exhibit significantly different optoelectronic properties from 3D metal halide perovskites (MHPs) due to their unique quantum confinement effects and large exciton binding energies. In particular, LDMHPs often have excellent broadband luminescence from self-trapped excitons. Chemical composition, hydrogen bonding, and external factors (temperature and pressure etc.) determine structures and influence photoelectric properties of LDMHPs greatly, and especially it seems that there is no definite regulation to predict the structure and photoelectric properties when a random cation, metal, and halide is chosen to design a LDMHP. Therefore, this review discusses the construction strategies of the recent reported LDMHPs and their application progress in the luminescence field for a better understanding of these factors and a prospect for LDMHPs' development in the future.

1. Introduction

As promising photoelectric materials, metal halide perovskites (MHPs) have been widely studied and applied to photovoltaic devices, photodetectors, light emitting diodes (LEDs), etc.^[1] In particular, MHPs have unique structure tunability, the FA⁺, MA⁺, or Cs⁺ in 3D MHPs replaced by larger sized organic cations

Dr. Y. Han, S. Yue, Prof. B.-B. Cui Advanced Research Institute of Multidisciplinary Science Beijing Institute of Technology (BIT) Beijing 100081, P. R. China E-mail: cui-chem@bit.edu.cn Dr. Y. Han Department of Materials Science and Engineering BIT Beijing 100081, P. R. China Dr. Y. Han, S. Yue, Prof. B.-B. Cui School of Materials Science and Engineering BIT Beijing 100081, P. R. China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/advs.202004805

O 2021 The Authors. Advanced Science published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/advs.202004805

can build various low-dimensional MHPs (LDMHPs) at the molecular level, such as 2D, 1D, and 0D metal halide crystal materials.^[2] 3D MHPs (ABX₃ A stands for monovalent cation, such as FA+, MA+, Cs+; M represents metal ions, such as Pb2+, Sn^{2+} , Ge^{2+} etc., and X stands for halogen ion Cl⁻, Br⁻, I⁻)^[3] with the advantages of high absorption coefficient, adjustable optical bandgap, low exciton binding energy, and long carrier diffusion distance have been widely used in the field of solar cells with a certified power conversion efficiency (PCE) of world recorded over 25%.[4] In general, 3D perovskites have small exciton binding energies ($\approx 20-50$ meV),^[5] which lead to their low radiation recombination efficiency and photoluminescent quantum efficiency (PLQE), and limit their application in luminescence.^[6] On the contrary, LDMHPs commonly exhibit excellent luminescence due to their quantum confined

effect and large exciton binding energies.^[7] Different from nanosheets, nanowires, and quantum dots at the structural level, LDMHPs discussed in this work refer to the low-dimensional crystals at the molecular level in particular.

The selection of cations, metals, and halogens play a key role in determining chemical composition and crystal structures of LDMHPs. Crystals with different dimensions were constructed by selecting the size of organic cations, and regulating metal cations could also construct LDMHPs with different dimensions.^[8] In addition to single metal, double perovskite, and quadruple perovskites could be formed by mixing metal cations.^[9] The change of halogen could regulate the configuration and the distortion degree of LDMHPs, which is the key to realize the broadband white luminescence.^[10] Generally, controlling growth of all-inorganic Cs-Pb-X perovskites with different dimensions could be easily realized by regulating the stoichiometric ratio of the precursor solution during the crystal growth progress.^[11] However, for organic-inorganic hybrid perovskites, a kind organic cation usually only constructed a structure even the stoichiometric ratio of every elements in the precursor solution was changed unless it formed different valence states or interacted with other molecules. On the other hand, manipulating the hydrogen bonding interactions between the inorganic skeletons and organic cations could significantly affect the orientation and conformation of inorganic skeleton.^[12] Furthermore, external pressure and temperature will provide thermodynamic energies to change the structures and photoelectric properties of LDMHPs.^[13,14]



Figure 1. a) Typical single crystal structures of 0D–3D organic–inorganic hybrid perovskites. 3D. Reproduced with permission.^[15] Copyright 2018, Wiley-VCH. b) 2D. Reproduced with permission.^[17] Copyright 2014, American Chemical Society. c) 1D. Reproduced with permission.^[19] Copyright 2017, Springer Nature. d) 0D. Reproduced with permission.^[12] Copyright 2019, Springer Nature.

Recently, it has spawned the "diamond fever" on the family of LDMHPs, and they have been intensely studied and applied as promising new photoelectric functional materials due to excellent luminescence properties and good stabilities.^[15] In particular, LDMHPs exhibit typical luminescent properties of large stokes shift and broadband emission,^[16] which could achieve tunable luminescence covering the whole visible light region and single phase white light emission.^[17] Compared to 3D perovskites, the summarization on the structural design strategy and its relationship with photoelectric properties of LDMHPs are still very rare. In this article, the specific discussion on the construction strategies related to alteration of chemical constituents including cations, metal ions, halide anions, stoichiometric ratio, hydrogen bonding, temperature, and pressure will be mainly reviewed. In addition, LDMHPs' broadband emissions and their application in LED devices and phosphors in solid lighting are discussed here to have a systematic and prospective knowledge of promotion in luminescence properties when different structures of LDMHPs are selected.

2. Structure Construction and Luminescence Performance

2.1. Cations

As shown in Figure 1a, the common structure of the 3D perovskite is AMX₃, in which the metal atoms are in the center and the halogen atoms are in the vertexes of the unit octahedrons extending in a 3D mode. The organic or inorganic monovalent cations are located in the cavities constructed by [MX₆⁴⁻] octahedrons, which is conforming to the theoretical formula of $RA + RX = t\sqrt{2(RM + RX)}$, where R_A , R_M , and R_X represent the radius of the A, M, X ions and t is the tolerance factor, respectively. For example, result from the construction formula limit, when t = 1, $R_{\rm M}$ and $R_{\rm x}$ are the maximum values ($R_{\rm Pb} = 1.19$ Å, $R_1 = 2.20$ Å), the maximum R_A approximately is 2.6 Å. Therefore, only small cations which maximum lengths are shorter than 2.6 Å can satisfy the condition to build 3D APbI₃ perovskites.^[18] Correspondingly, replacing the FA⁺, MA⁺, or Cs⁺ with larger size organic cations, abundant LDMHPs can be obtained, including layered 2D, linear 1D and points distributed 0D metal halide hybrids (Figure 1b-d).

The size of cations affects the connection modes of lead halide octahedrons. There are three types of connection modes for

metal halide perovskites: corner-sharing, edge-sharing, and facesharing as shown in Figure 2a. Although most configurations of 2D perovskites are corner-sharing, a few 2D perovskites have broken the conventional connection mode and formed edge-sharing and face-sharing structures. The types of connection modes can be regulated by changing the length of amines.^[7] For example, as shown in Figure 2b–e, $C_6H_5(CH_2)_nNH_3^+$, where n = 1, 2, 3, 4 represents organic phenylammonium (PMA), phenylethylammonium (PEA), phenylethylammonium (PPA), and phenylethylammonium (PBA), respectively. The 2D structures constructed by PMA and PEA are corner-sharing, while the 2D structures constructed by the longer PPA and PBA are corner-sharing and face-sharing coexistence.^[20] Recently, the post-perovskite with edge-sharing structure formed by organic cation trans-2, 5dimethylpiperazine has been reported. Due to the distorted inorganic lead halogen structure, it exhibits white emission with a high PLQE.^[21] Furthermore, the connection mode influences the orbital overlap between metals and halogens, thus affecting the bandgap values of 2D perovskites, where it is common that facesharing>edge-sharing>corner-sharing for bandgap values.[7]

For common 2D perovskites, organic cations which are suitable for 2D interlayer frames often contain a positive charge (e.g., RNH_3^+ , $R_2NH_2^+$, R_3NH^+ , R_4N^+ (R is a paraffinic chain)); hydrogen atoms of the organic amine can interact with halide atoms on metal halide octahedrons by hydrogen bonding. The distance between the inorganic layers in 2D perovskites can be adjusted by organic cations with short or long paraffinic chains, and perovskites in lower dimensions can be obtained by adjusting longer paraffinic chains. For example, 2D perovskites (R_nNH₃)₂MX₄ and (NH₃R_nNH₃)MX₄ constructed by monoamine and diamine organic cations are shown in Figure 4. For $(R_n NH_3)_2 MX_4$, when n = 1, methylamine cation construct the common 3D perovskite MAPbX₃,^[22] and when n = 2, ethylamine, it construct the 2D perovskites EA₄Pb₃X₁₀.^[10] EA has two configurations in two positions, as some of the cations are filled into 3D perovskite cavity and another part of the EA that splits into inorganic layer to form a 2D perovskite. In addition, when n > 2, the organic cations will construct single layer 2D perovskites.^[23] For (NH₃R₂NH₃)MX₄, the diamine organic cations are long enough to link the two inorganic layers as the n values increases. For example, when $n \ge n$ 4, such as $[NH_3(CH_2)_n NH_3]PbI_4$ (n = 4, 6, 8), the diamine organic cations are long enough to construct regular 100-oriented 2D perovskites.^[24] The other good example is that, for butyric diamine (n = 4), propylene diamine (n = 3), and ethylenediamine (n = 2), as the length of the amine chain decreases, the layered







Figure 2. a) 2D structure of corner-sharing, edge-sharing and face-sharing. Reproduced with permission.^[7] Copyright 2019, American Chemical Society. b–e) 2D perovskites constructed by PMA, PEA, PPA, and PBA, respectively. Reproduced with permission.^[20] Copyright 2016, American Chemical Society.



Figure 3. a) Structure of 1D organic lead halide perovskites $C_4N_2H_{14}PbBr_4$ constructed by $C_4N_2H_{14}^{2+}$. Reproduced with permission.^[19] Copyright 2017, Springer Nature. b) Preparation of 28% white light emission system with 1D $C_4N_2H_{14}PbBr_4$ doping Mn^{2+} . Reproduced with permission.^[26] Copyright 2017, American Chemical Society c) Structure of 1D organic lead halide perovskites $C_4N_2H_{14}PbBr_4$. Reproduced with permission.^[27] Copyright 2018, American Chemical Society. d) 1D Sn-based $C_4N_2H_{14}SnBr_6$ transformed into a 0D structure ($C_4N_2H_{14}Br$)₄SnBr₆. Reproduced with permission.^[28] Copyright 2017, Wiley-VCH. e) Structure of core–shell 0D perovskites ($C_4N_2H_{14}X$)₄S_nX₆ (X = Br, I). Reproduced with permission.^[29] Copyright 2018, RoyalSociety of Chemistry.

perovskite changes from a 100-oriented flat layer to a distorted layer, and then when n = 2, the layer broken to construct a 1D ribbon structure.^[25]

Recently, Ma's group synthesized multiple perovskites with 1D and 0D structures by diamine cation with the N, N-2-dimethylethylenediamine (organic cation 17 in Figure 4).

Such as the 1D $C_4N_2H_{14}PbBr_4$ with efficient bluish whitelight emission,^[19] as shown in **Figure 3a**. The $C_4N_2H_{14}PbBr_4$ achieved white light emission with PLQE of 28% by doping Mn^{2+} (Figure 3b).^[26] The author also reported 1D perovskite $C_4N_2H_{14}PbCl_4$ (Figure 3c) and studied its structure distortion.^[27] As shown in Figure 3d, from no luminescence property to







Figure 4. The reported organic molecules with large cross-sectional area for constructing 1D and 0D perovskites (Ref: $1,^{[30]} 2,^{[29]} 3,^{[33]} 4,^{[34]} 5,^{[35]} 6,^{[12]} 7,^{[36]} 8,^{[37]} 9,^{[38]} 10,^{[39]} 11,^{[40]} 12,^{[41]} 13,^{[42]} 14,^{[43]} 15,^{[44]} 16,^{[24]} 17,^{[29]} 18,^{[12]} 19,^{[23]} 20,^{[10]} 21,^{[45]} 22,^{[46]} 23,^{[47]} 24,^{[48]} 25,^{[25]} 26,^{[25]} 27,^{[17]}$).

yellowish-white emission, 1D Sn-based $C_4N_2H_{14}SnBr_6$ is easier to transform into a 0D of $(C_4N_2H_{14}Br)_4SnBr_6$.^[28] And the Sn-based 0D $(C_4N_2H_{14}X)_4SnX_6$ (X = Br⁻, I⁻) has a PLQE of nearly unity (Figure 3e).^[29]

Although the organic cations in 2D structure are not as small as the cations in 3D perovskites, they still need to fit into the frame of 2D inorganic layers, and the cross-sectional area of organic molecule must be suitable to the square range constructed by the four corner-sharing lead halide octahedrons, allowing the organic molecule to tilt and interlace, where the side length of the square is greater than or equal to twice the average bond length of the Pb-X. The space cannot accommodate the too large adjacent organic molecules, because the larger cations more possibly construct lower dimensional structures, such as 1D and 0D structures. For organic molecules with large cross-sectional area, it's more likely to break up the 2D inorganic layers to form a 1D or 0D structure. For example, the large circular organic molecules $C_9NH_{20}^+$ (organic cation 2 in **Figure 4**) constructed a variety of 0D MHPs, such as $(C_9NH_{20})_7$ (PbCl₄)Pb₃Cl₁₁ with a blue emission,^[31] $(C_9NH_{20})_2$ SnBr₄ with a deep-red emission,^[32] $(C_9NH_{20})_2$ SbCl₅ with a yellow emission,^[29] and (bmpy)₉[ZnCl₄]₂[Pb₃Cl₁₁]^[12] with a green emission, etc. Organic cations with large cross-sectional area in 1D and 0D structures are summarized in Figure 4, and the optical properties of these LDMHPs constructed by corresponding molecules are shown in **Table 1**. In summary, the size of the organic cations plays a key role in constructing LDMHPs' structures.

(Ph ₄ P) ₂ SbCl ₅	Ν/Δ				
	11/1	Antisolvent method	648	136	87
(C ₉ NH ₂₀) ₂ SbCl ₅	N/A	Antisolvent method	590	119	98± 2
(C ₉ NH ₂₀) ₇ (PbCl ₄)Pb ₃ Cl ₁₁	Face-sharing	Antisolvent method	470	84	83
(C ₉ NH ₂₀) ₂ S _n Br ₄	N/A	Solution method	695	146	46
(bmpy) ₉ [ZnCl ₄] ₂ [Pb ₃ Cl ₁₁]	Face-sharing	Antisolvent method	470	≈50	83
(C ₄ H ₈ N ₂ H ₄) ₂ PbBr ₆ ·2H ₂ O	Corner-sharing	Cooling crystallization	N/A	N/A	N/A
(C ₁₃ H ₁₉ N ₄) ₂ PbBr ₄	N/A	Antisolvent method	460	66	40
$(C_6N_2H_{16}CI)_2SnCl_6$	N/A	Solution method	450	125	8.1
(C ₃ N ₃ H ₁₁ O) ₂ PbBr ₆ ·4H ₂ O	N/A	Antisolvent method	568	200	9.6
(C ₆ H ₈ N ₃) ₂ Pb ₂ Br ₁₀	Corner-sharing	Cooling crystallization	580	≈200	9
[(AD)Pb ₂ Cl ₅]	Corner-sharing	Solution method	533	N/A	7.45
[Nmethyldabconium]PbI ₃	Face-sharing	Solution evaporation	469	N/A	N/A
(C ₆ H ₁₃ N ₄) ₃ Pb ₂ Br ₇	Face-sharing	Antisolvent method	580	158	7
C ₅ H ₁₄ N ₂ PbCl ₄ ·H ₂ O	Edge-sharing	Cooling crystallization	412, 617	N/A	N/A
[C ₆ H ₁₄ N]PbI ₃	Face-sharing	Solution evaporation	675	N/A	N/A
	$(C_9 NH_{20})_7 (PbCl_4) Pb_3 Cl_{11}$ $(C_9 NH_{20})_2 S_n Br_4$ $(bmpy)_9 [ZnCl_4]_2 [Pb_3 Cl_{11}]$ $(C_4 H_8 N_2 H_4)_2 PbBr_6 \cdot 2H_2 O$ $(C_{13} H_{19} N_4)_2 PbBr_4$ $(C_6 N_2 H_{16} Cl)_2 SnCl_6$ $(C_3 N_3 H_{11} O)_2 PbBr_6 \cdot 4H_2 O$ $(C_6 H_8 N_3)_2 Pb_2 Br_{10}$ $[(AD) Pb_2 Cl_5]$ $[Nmethyldabconium] PbI_3$ $(C_6 H_{13} N_4)_3 Pb_2 Br_7$ $C_5 H_{14} N_2 PbCl_4 \cdot H_2 O$ $[C_6 H_{14} N] PbI_3$ anighlighted in blue refers to the comparison of the set of the		$(C_9NH_{20})_7$ (PbCl ₄)Pb ₃ Cl ₁₁ Face-sharingAntisolvent method $(C_9NH_{20})_2S_RBr_4$ N/ASolution method $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ Face-sharingAntisolvent method $(C_4H_8N_2H_4)_2PbBr_6\cdot 2H_2O$ Corner-sharingCooling crystallization $(C_13H_{19}N_4)_2PbBr_4$ N/AAntisolvent method $(C_6N_2H_{16}Cl)_2SnCl_6$ N/ASolution method $(C_6H_8N_3)_2Pb_2Br_10$ Corner-sharingCooling crystallization $(C_6H_8N_3)_2Pb_2Br_{10}$ Corner-sharingCooling crystallization $[(AD)Pb_2Cl_5]$ Corner-sharingSolution method $(C_6H_{13}N_4)_3Pb_2Br_7$ Face-sharingSolution evaporation $(C_6H_{13}N_4)_3Pb_2Br_7$ Face-sharingCooling crystallization $(C_6H_{14}N_4)_9Pb1_3$ Face-sharingSolution evaporation $(C_6H_{14}N_4)PbL_4 \cdot H_2O$ Edge-sharingCooling crystallization $[C_6H_{14}N]Pb1_3$ Face-sharingSolution evaporation	$(C_9 N H_{20})_7 (PbCl_4) Pb_3 Cl_{11}$ Face-sharingAntisolvent method470 $(C_9 N H_{20})_2 S_n Br_4$ N/ASolution method695 $(bmpy)_9 [ZnCl_4]_2 [Pb_3 Cl_{11}]$ Face-sharingAntisolvent method470 $(C_4 H_8 N_2 H_4)_2 PbBr_6 \cdot 2H_2 O$ Corner-sharingCooling crystallizationN/A $(C_1 H_1 P N_4)_2 PbBr_4$ N/AAntisolvent method460 $(C_6 N_2 H_1 6 Cl)_2 Sn Cl_6$ N/ASolution method450 $(C_3 N_3 H_{11} O)_2 PbBr_6 \cdot 4H_2 O$ N/AAntisolvent method568 $(C_6 H_8 N_3)_2 Pb_2 Br_{10}$ Corner-sharingCooling crystallization580 $[(AD) Pb_2 Cl_5]$ Corner-sharingSolution method533[Nmethyldabconium]PbI_3Face-sharingSolution evaporation469 $(C_6 H_1 N_4)_3 Pb_2 Br_7$ Face-sharingCooling crystallization580 $(C_5 H_1 A_1 N_2 PbCl_4 \cdot H_2 O)$ Edge-sharingCooling crystallization412, 617 $[C_6 H_1 N_4) PbL_3$ Face-sharingSolution evaporation412, 617	$(C_9NH_{20})_7$ (PbCl ₄)Pb ₃ Cl ₁₁ Face-sharingAntisolvent method47084 $(C_9NH_{20})_2S_RBr_4$ N/ASolution method695146 $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ Face-sharingAntisolvent method470 ≈ 50 $(C_4H_8N_2H_4)_2PbBr_6\cdot 2H_2O$ Corner-sharingCooling crystallizationN/AN/A $(C_13H_{19}N_4)_2PbBr_4$ N/AAntisolvent method46066 $(C_6N_2H_16Cl)_2SnCl_6$ N/ASolution method450125 $(C_3N_3H_{11}O)_2PbBr_6\cdot 4H_2O$ N/AAntisolvent method568200 $(C_6H_8N_3)_2Pb_2Br_{10}$ Corner-sharingCooling crystallization580 ≈ 200 $[(AD)Pb_2Cl_5]$ Corner-sharingSolution method533N/A[Nmethyldabconium]Pbl ₃ Face-sharingSolution evaporation469N/A $(C_6H_{13}N_4)_3Pb_2Br_7$ Face-sharingCooling crystallization580158 $C_5H_{14}N_2PbCl_4\cdotH_2O$ Edge-sharingCooling crystallization412, 617N/A $(C_6H_{13}N_4)_3Pb_2Br_7$ Face-sharingSolution evaporation412, 617N/A $(C_6H_{14}N_1Pbl_3)$ Face-sharingSolution evaporation675N/A

2.2. Metal lons

Most 2D perovskites are in (NH₄RNH₄)MX₄ and (RNH₄)₂MX₄ structures, where M is usually a divalent metal, e.g., Pb²⁺, Sn²⁺, Ge²⁺, Mn²⁺, Fe²⁺, Co²⁺, Cu²⁺. Here, Sn²⁺ and Ge²⁺ are often introduced to replace toxic Pb²⁺ in perovskites, but their stability is very poor, as the Sn²⁺ and Ge²⁺ ions are easily oxidized to Sn⁴⁺ and Ge⁴⁺.^[49] Recently, the Cu²⁺ based perovskites have attracted attention due to their good stability, such as the 2D 100-oriented perovskite MA₂CuCl_{4-x}Br_x prepared by MA cations.^[54] In addition, a series of 2D perovskites with different organic cations including (C₄H₉NH₃)₂CuBr₄,^[55] (C₅H₉NH₃)₂CuBr₄,^[56] (C₆H₅CH₂CH₂NH₃)₂CuCl₄,^[57] and (C₄H₉NH₃)₂MCl₄ (M = Mn, Cu, Cd, Pb),^[59] (CnH_{2n+1}NH₃)₂MCl₄ (M = Mn, Fe, Co, Cu, Zn, and *n* = 2, 4, 6, 8, 10, 12), ^[60] etc. have been reported. Recently, the layered double perovskite

 $Cs_4CuSb_2Cl_{12}$ with two metal ions (Cu^{2+} and Sb^{3+}) was synthesized for the first time.^[50] As shown in **Figure 5**a, the number of inorganic layers regulation of this material has been realized, which initiated a new chemical component design strategy to regulate the layers of 111-oriented 2D perovskites. It's worth mentioning that Bi metals formed the 0D structures, such as $(CH_3NH_3)_3Bi_2I_9$ (Figure 5b) with Bi^{3+} ,^[51] and $ABiBr_6$ ($A = Cs^+$, MA^+ , FA^+ , $C_3H_9N^+$, BA^+ , $C_5H_6N^+$, $C_7H_7^+$, *N*-EtPy⁺) with Bi^{5+} (Figure 5c).^[52] It has been reported that for 0D double perovskite (C_8NH_{12})_4 $Bi_{0.57}Sb_{0.43}Br_7$ ·H₂O (Figure 5d),^[53] the individual [$BiBr_6$]³⁻ and [$SbBr_6$]³⁻ octahedrons are completely isolated and surrounded by large organic $C_8H_{12}N^+$, and so they have exhibited a great stability.

The diversified options of metal ions can not only construct the double perovskites,^[9] but also theoretically design the structure of quadruple perovskites. For example, Lin et al. propose a strategy to design quadruple perovskites by introducing heterovalent cation to form double perovskites. And these two stable quadruple perovskite halides of $Cs_4CdSb_2Cl_{12}$ and $Cs_4CdBi_2Cl_{12}$ with vacancy-ordered structures were successfully synthesized by solvent heat method and exhibited broadband emissions.^[61] **Figure 6** shows the design diagram of quadruple perovskite, the quadruple perovskites provide a promising design method for structure regulation of perovskites.

2.3. Halogens

Halogens have great influence on the structures of LDMHPs, too. For example, Dohner et al. reported 2D perovskites (EDBE)[PbX₄] (X = Cl⁻, Br⁻, I⁻)^[17] with white emissions. Crystal structures of these materials are shown in **Figure 7**, in which the Pb-Cl is a 100oriented structure. When the lead halide octahedron is deformed due to the different coordination environment of Pb²⁺, the 2D perovskites of Pb-Br and Pb-I became 110-oriented structures. Kanatzidis et al. reported 2D hybrid perovskites of EA₄Pb₃X₁₀ (X = Cl⁻, Br⁻),^[10] and when the halogen is I⁻, it did not form an analogue with EA₄Pb₃X₁₀ (X = Cl⁻, Br⁻), but a 1D face-sharing perovskite.

Halogens affect structure distortions of LDMHPs significantly. As the ion radius of Cl^- (1.67 Å) is less than that of Br^- (1.82 Å), it does not accommodate the EA⁺ cation well and so the EA₄ Pb₃Cl₁₀ has highly distorted structure.^[62] For EA₄Pb₃Br₁₀, the intermediate layer of Pb-Br is of regular structure, while the outer layer Pb-Br has obvious structural distortion (Figure 8a). The distortion of intrinsic structure affects the luminescence characteristics of LDMHPs. That the effect of halogen replacement on structure distortion and luminescence properties have many examples and broadband emission is strongly associated with distorted degrees of lattices in LDMHPs. Mao et al.^[10] found that different distortion levels in EA₄Pb₃Cl₁₀ (large distortion) versus EA₄Pb₃Br₁₀ (small distortion) and EA4Pb3Cl10 has a broadband white-light emission, while $EA_4Pb_3Br_{10}$ has a narrow blue emission. By further tuning the ratio of chlorine/bromine for $EA_4Pb_3Br_{10-x}Cl_x$ (x = 0, 2, 4, 6, 8, 9.5, 10), they found that two of the





Figure 5. a) The regulation of layers is realized in 2D double perovskite $Cs_4CuSb_2Cl_{12}$. Reproduced with permission.^[50] Copyright 2018, Wiley-VCH. b) Structure of 0D perovskites $(CH_3NH_3)_3Bi_2l_9$. Reproduced with permission.^[51] Copyright 2017, American Chemical Society. c) Structure of 0D perovskites ABiB₆. Reproduced with permission.^[52] Copyright 2018, American Chemical Society. d) Lead-free 0D double perovskite $(C_8NH_{12})_4Bi_{0.57}Sb_{0.43}Br_7 \cdot H_2O$. Reproduced with permission.^[53] Copyright 2019, Wiley-VCH.



Figure 6. Design schematic diagram of cation mutations from simple perovskites to double perovskites and quadruple perovskites. Reproduced with permission.^[61] Copyright 2019, American Chemical Society.

intermediate compounds (x = 8 and 9.5) have more optimized white-light emissions than that of pure EA₄Pb₃Cl₁₀ (Figure 8b). Yangui et al.^[63] studied (C₆H₁₁NH₃)₂[PbBr₄] and

 $(C_6H_{11}NH_3)_2[PbI_4]$ with similar structures, in which the $[PbI_6]^{4-}$ is more regular than [PbBr₆]⁴⁻ octahedron. Figure 8c shows the PL variation of $(C_6H_{11}NH_3)_2$ [PbBr_{4-x}I_x] with mixed halogens. The full width at half-maximum (FWHM) of PL gradually widened with the decrease of I- content due to the difference of structure distortions. Furthermore, halogens can also tune structure distortion through hydrogen bonding formed between organic cations and halide anions. Here, different electronegative properties of halogens lead to different strength of hydrogen bonding force (where H-Cl > H-Br > H-I), determining the orientation of organic cation^[18] in interlayer of metal halides and caused different distortion degrees of lead halide octahedron. Furthermore, the halogens can be replaced by other anions, such as the SCN⁻ which has a similar radius with I⁻. The 100-oriented 2D perovskite (CH₃NH₃)₂Pb(SCN)₂I₂^[64] can be obtained by partially replacing the I⁻ with SCN⁻. Its structure is shown in Figure 8d, in which the lead coordination octahedron is constructed by four equatorial I⁻ and two axial SCN⁻ coordination. Due to the polarity of SCN⁻, the octahedron is distorted by Pb–S bonds.^[65]

2.4. Hydrogen Bonding

The all-inorganic Cs-M-X structures (M = Pb²⁺, Sn²⁺, Ge²⁺ etc., $X = Cl^-$, Br⁻, I⁻) are mainly constructed by electrostatic effects

www.advancedsciencenews.com



www.advancedscience.com



Figure 7. Structure of (EDBE)[PbX₄] (X = Br and Cl) crystal structure. Reproduced with permission.^[17] Copyright 2014, American Chemical Society.



Figure 8. a) Structure diagram of $EA_4Pb_3X_{10}$ (X = Br and Cl) (where the inner layers are "undistorted" octahedra and the outer layers are composed of "distorted" octahedra). b) The mixed halogen $EA_4Pb_3Br_{10-x}Cl_x$ (x = 0, 2, 4, 6, 8, 9.5, 10) crystals. a,b) Reproduced with permission.^[10] Copyright 2019, American Chemical Society. c) PL of $(C_6H_{11}NH_3)_2$ [PbBr_{4-x}l_x] vary with the content of I. Reproduced with permission.^[63] Copyright 2017, Elsevier B.V. d) Structure of 2D perovskite $(CH_3NH_3)_2Pb(SCN)_2I_2$. Reproduced with permission.^[64] Copyright 2017, Royal Society of Chemistry.

between negatively charged metal halide octahedrons and positively charged Cs⁺. For organic–inorganic hybrid perovskites, organic cations contain one or more terminal amines in which H atoms interacting with halogens on inorganic octahedrons by hydrogen bonding. For example, the 110-oritented 2D perovskites have been widely studied recently due to their excellent white emission properties, and their unique corrugated structures are stabilized by hydrogen bonding. For example, Kanatzidis et al.^[45] reported the corrugated 2D perovskite (DMEN)PbBr₄, as is shown in **Figure 9a**. Its 3×3 corrugated layer configuration is stabilized by hydrogen bonding. With H atoms on the primary and secondary amines of organic cations forming hydrogen bonding with Br atoms, the inorganic layer folds \approx 90°, producing the strongly corrugated structure (Figure 9b). In addition, many other corrugated 2D structures, such as (*N*- MEDA)[PbBr₄]^[17] which is shown in Figure 9c have been reported. It exhibits a white emission upon UV light with a high PLQE of 9% (Figure 9d). (Epz)PbBr₄ (Figure 9e)^[66] is another example to demonstrate the role of hydrogen bonding in stabilizing the 110-oriented 2D perovskites (Figure 9f).

In fact, the formation of hydrogen bonding plays a decisive role in regulating the orientation and conformation of inorganic skeleton. Different amines, such as primary amines, secondary amines, tertiary amines all can construct metal halides 1D structures with different interlinkage modes (**Figure 10**a),^[43] and the organic cations 1, 2, and 3 containing different N-H sites which are adjacent, interphase and pair sites constructed 2D, 1D, and 0D configurations, respectively (Figure 10b).^[67] The structures of (GUA)₂PtI₆ and (FA)₂PtI₆^[68] are shown in Figure 10c, and here the discrete [PtI₆]^{4–} octahedrons are connected by 3D hydrogen







Figure 9. a) The 3 × 3 corrugated layer structure of α -(DMEN)PbBr₄ and b) its hydrogen bonds schematic diagram. a,b) Reproduced with permission.^[45] Copyright 2017, American Chemical Society. c) Structure of corrugated 2D perovskite (*N*-MEDA)[PbBr₄]. d) The perovskite (*N*-MEDA)[PbBr₄] under the irradiation of ultraviolet lamp shows bright white light. c,d) Reproduced with permission.^[17] Copyright 2014, American Chemical Society. e) Structure of (epz)PbBr₄ and f) hydrogen bonding diagram. e,f) Reproduced with permission.^[66] Copyright 2018, American Chemical Society.

bonding network constructed by FA²⁺ and the 2D network constructed by GUA²⁺ cations, indicating that the hydrogen bonding force of organic cations affect the arrangement of inorganic [PtI₆]⁴⁻ octahedrons. Recently, Cui et al. reported the structure transition from the corrugated 1D structure to 0D by adjusting hydrogen bonding (Figure 10d,e). By employing a unique ureaamide cation containing $H_4N-C=O$, which can form multiple hydrogen bonds between adjacent organic cations and inorganic skeleton. The corrugated 1D structure was stabilized by the hydrogen bonding of Pb-Br···H-N. When increase the concentration of amides in the growth process of crystals, the amides will form hydrogen bonds with H₂O in precursor solution and adjacent cations to construct a large network (Figure 10f), which completely separated the [PbBr₆]⁴⁻ octahedrons to form a 0D perovskite. The 1D and 0D perovskites both exhibited stable white emission, and the dimension reduction from 1D to 0D increased the PLQE as much as five times, providing a new strategy to regulate the structure and improve the luminescence performance by regulating hydrogen bonding forces in MHPs.^[12]

2.5. Stoichiometric Ratio of Precursor Solution

For all-inorganic Cs-Pb-X perovskite crystals, different structure dimensions can be easily regulated by changing the stoichiometric ratio of precursor solution. For example, a ternary phase diagram of 1D Cs₄PbBr₆, 2D CsPb₂Br₅, and 3D CsPbBr₃ is shown in **Figure 11**a, in which dimension regulation is achieved by stoichiometric ratio (CsBr:PbBr₂) control. As shown in Figure 11b, the traditional 3D structure of CsPbBr₃ has two phases, cubic phase (Pm3m) and orthorhombic phase (Pnma). When PbBr₂ is abundant, 2D structure $CsPb_2Br_5$ is formed,^[69] and Cs⁺ ions appear between the inorganic layers. In contrast, when CsBr is excess, 0D structure Cs_4PbBr_6 is formed, of which individual lead halide octahedrons are completely separated by Cs⁺.^[70] The bandgaps of these Cs-Pb-Br perovskites increase with the dimension decreasing (Figure 11c). Both CsPbBr₃ and Cs₄PbBr₆ showed direct bandgap, while CsPb₂Br₅ showed indirect bandgap. The Cs-Pb-I perovskites can also construct different dimensions by controlling the stoichiometric ratio of CsI versus PbI₂.

For organic-inorganic hybrid perovskites, a kind of organic cation usually constructed a kind of structure even the stoichiometric ratio of every elements in the precursor solution changed. However, when cations form different valence states in crystals, multiple dimensional structures, such as the 2D μ -IPA₃Sn₂I₇ and 1D θ -IPA₂SnI as shown in Figure 12a can be built.^[71] On the other hand, different single crystal structures can also be obtained when H₂O molecules grow into unit cells. For example, Cui et al. synthesized the 1D (C₃N₃H₁₀O)(C₃N₃H₁₁O)₂Pb₂Br₉ with the ratio of $C_3N_3H_9O\cdot 2HBr$: PbO = 3 : 2, and when the ratio increased to 2 : 1, H₂O entered into the unit cell to form a 0D ($C_3N_3H_{11}O$)₂PbBr₆·4H₂O.^[12] Recently, Thomas T. M. et al. reported the well-known 100-oriented 2D (C₆H₅CH₂NH₃)₂PbI₄ phase with a corner-sharing structure, and a new compound 1D edge-sharing (C₆H₅CH₂NH₃)₄Pb₅I₁₄·2H₂O was generated when H₂O incorporated into the crystal structure (Figure 12b).^[72] Furthermore, H₂O molecules improved LDMHPs' luminescent properties. Lin et al. has synthesized two new 0D (C₆N₂H₁₆)SbCl₅ and (C₆N₂H₁₆)SbCl₅·H₂O, in which H₂O molecules grew into





www.advancedscience.com



Figure 10. a) Different kinds of amines, primary amines, secondary amines, tertiary amines constructed 1D structures with different interlinkage modes. Reproduced with permission.^[43] Copyright 2011, Elsevier B.V. b) Organic cations at different sites and constructed 2D structure (H22-AMP)PbBr₄(1), 0D structure (H23-AMP)₂PbBr₆(2), and 1D structure (H24-AMP)PbBr₄ (3). Reproduced with permission.^[67] Copyright 2007, Elsevier Masson SAS. c) Structure of (GUA)₂PtI₆, (FA)₂PtI₆ and their hydrogen bonds schematic diagram. Reproduced with permission.^[68] Copyright 2018, American Chemical Society. Structures of d) 1D (C₃N₃H₁₀O) (C₃N₃H₁₁O)₂Pb₂Br₉ and e) 0D (C₃N₃H₁₁O)₂PbBr₆·4H₂O, respectively. f) View of hydrogen-bonding in organic cations and water of the bulk 0D lead bromide crystal. Reproduced with permission.^[12] Copyright 2019, Springer Nature.

lattices of $(C_6N_2H_{16})SbCl_5 \cdot H_2O$ leading to the larger spatial distance between the $[SbCl_5]$ dimers (Figure 12c) and improving the PLQE of 57%.^[73] In addition, dimethylsulfoxide (DMSO) molecules also can be introduced to crystals to build different dimensional structures, such as the 0D (PDI)₂PbI₂ and 1D (PDI)₂PbI₂·2DMSO (Figure 12d).^[74]

2.6. Temperature Effect

Perovskite materials usually undergo phase transition when the temperature changes, which are mainly caused by changes in configurations of organic cations. For example, the organic cations were disorderly arranged as the temperature increased (> 300 K) and the disordered point was called the melting temperature.^[75] The disordered cations led to sudden change of 2D interlayer distance and lattice parameters along the direction of organic cations.^[76] Recently, Zeb et al.^[77] synthesized a 1D perovskite crystal 1-methylpiperidinium triiodoplumbate(II) (MPIP). They found the MPIP had an obvious phase transformation near the Tc = 202 K due to the ordered-disordered transition of 1-methylpiperidinium cation (**Figure 13**a). In addition, Liao's group^[78] synthesized a 1D [C₆H₁₁NH₃]₂CdCl₄ with high temperature dielectric response, due to it undergoes the phase transition at 367 K caused by the change of relative position of Cd atoms (Figure 13b).

Temperature not only affects LDMHPs' structures, but also causes difference in their photoelectric properties. For example, Eric et al. studied the exciton characteristics of 2D $(C_4H_9NH_3)_2PbI_4$ in a temperature range of 10–300 K.^[79] Under the drive of $C_4H_9NH_3^+$ rearrangement, phase transition occurred at around 250 K, corresponding to the decrease of lattice spacing and the increase of exciton binding energy. In addition, Sieradzki et al.^[14] synthesized a 2D (MHy_2PbI_4) as shown in Figure 13c. With the temperature decreasing, MHy_2PbI_4 underwent three structure phase transition at 320, 298, and 262 K, respectively. The second phase transition at 298 K was related to the arrangement of MHy⁺, and this phase transition caused a significant change in the dielectric constant. As shown in Figure 13d, the interlayer spacing between the inorganic layers increased

SCIENCE NEWS _____



www.advancedscience.com



Figure 11. a) The ternary phase of Cs-Pb-Br, proportion of precursor solution (CsBr and PbBr₂). b) Conversion between (CsPbBr₃, CsPb₂Br, and Cs₄PbBr₆). c) Electron band structure of CsPbBr₃, CsPb₂Br, and Cs₄PbBr₆. Reproduced with permission.^[11] Copyright 2018, American Chemical Society.

with the temperature increasing. In addition, the emission of MHy_2PbI_4 exhibited blueshift during cooling temperature from 300 to 80 K. It exhibited light yellow emission at 300 K and turned to yellow-green emission at 80 K (Figure 13e). The few-layer exfoliated 2D ($C_4H_9NH_3$)₂PbI₄ underwent phase transition at \approx 175 K, producing a new blueshift PL peak (**Figure 14a**).^[80] It is worth mentioning that temperature has a great influence on the emission from relaxed states of LDMHPs. These materials usually have emission from relaxed states caused by lattice distortion or self-trapped excitons (STEs). The PL intensity of relaxed states is more efficient than the free exciton (FE) at low temperatures.

Recently, RPP perovskite $(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)_{n-1}$ $Pb_nI_{3n+1}(n = \approx 1-4)$ has been reported,^[81] and it undergoes structure distortion under laser irradiation, resulting in a relaxed redshifted emission (Figure 14b). The relaxation peak increased sharply with the temperature decreasing (Figure 14c). In addition, the STE emission intensity also increased as the temperature decreased. Some 2D 100-oriented perovskites can observe STE emissions at low temperature (Figure 14d).^[82,48] When temperatures are high, the STEs are easy to detrap from STE states to FE states, and at low temperatures, the detrapping process is suppressed,^[82] Therefore, STEs emission gradually appears and increases at lower temperature.

2.7. Pressure Effect

Exerting high pressure to the material is an effective way to regulate structures and photoelectric properties of LDMHPs. For example, Liu et al.^[83] reported that 2D $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n = 3) reduced the bandgap by 8.2% after increasing the pressure. This is because external pressure enhanced coupling between s

orbitals of Pb atoms and p orbitals of I atoms. Yin et al.^[84] studied the mechanically exfoliated 2D layers of $(C_4H_9NH_3)_2PbI_4$ under pressure. As shown in **Figure 15**a, under initial compression from 1 atm to 0.5 GPa, the slight blueshifts of bandgap happened due to the decreased Pb–I–Pb bond angles. Perovskite lattices were compressed when pressure continued to increase, and the bond length of Pb–I–Pb inevitably decreased. This increased the overlap of electronic wave function of Pb and I atoms, and finally caused bandgap redshifts.

Shi's team^[13] synthesized a unique 1D organic tin bromide perovskite $C_4N_2H_{14}SnBr_4$. The 1D inorganic chain deformed under the transition from monoclinal phase to triclinic phase (Figure 15b), and the exciton binding energy increased, resulting in the enhancement of PL

intensity (Figure 15c). This work revealed a potential application of supercharging to improve the luminescence performance of LDMHPs. Zhang et al.^[85] studied the PL properties of 0D Cs₃Bi₂I₉ under high pressure. As shown in Figure 15d, under high pressure, the bandgap of Cs₃Bi₂I₉ continued to become narrow, and finally reached the optimal value. In addition, at atmospheric pressure, the isolated $[Bi_2I_9]^{3-}$ octahedron exhibited only weak emission upon excitation. But it exhibited significant enhancement of PL intensity about ten times under relatively high pressure (< 1 GPa) due to the increased exciton binding energy.

It is worth mentioning that external pressure could distort the structure of the LDMHP to produce its STE emission. Recently, it has been reported that the pressure effect on regulating the structure distortion achieving the STE emission of (BA)₄AgBiBr₈.^[86] With the increasing pressure, the emission of (BA)₄AgBiBr₈ changed from a nonluminescent state under atmospheric pressure to a state with obvious fluorescence at 2.5– 25.0 GPa (**Figure 16**a). The sample completely transformed to a



ADVANCED SCIENCE

www.advancedscience.com



Figure 12. a) The structures of 2D μ -IPA₃Sn₂I₇ and 1D θ -IPA₃Sn1. Reproduced with permission.^[71] Copyright 2017, American Chemical Society. b) The structures of 2D (C₆H₅CH₂NH₃)₂PbI₄ and 1D (C₆H₅CH₂NH₃)₄Pb₅I₁₄·2H₂O. Reproduced with permission.^[72] Copyright 2017, American Chemical Society. c) Diagram of organic cations ([C₆N₂H₁₆]⁺ or [C₆N₂H₁₆]·H₂O⁺) and 0D [SbCl₅] dimers. Reproduced with permission.^[73] Copyright 2020, Wiley-VCH. d) The structures of 1D (PI)₂PbI₂·2DMSO and 0D (PDI)₂PbI₂. Reproduced with permission.^[74] Copyright 2020, American Chemical Society.

new structure at 2.1 GPa (Figure 16b). In addition, the new structure gradually distorted and its crystallinity reduced upon compression. Finally, a completely lower crystallinity phase formed at around 25.0 GPa, which led to the quenching of the luminescence. The luminescence mechanism is shown in Figure 16c. Under atmospheric conditions, the STEs were easy to detrap and return to FE states. When the pressure increases, the structure distortion of $(BA)_4$ AgBiBr₈ deepens its self-trapped states, which enhanced the energy barrier to avoid the detrap of excitons. And the bright emission from self-trapping realized.

3. Luminescence Applications

3.1. Light-Emitting Diodes (LEDs)

Due to the size effect and significant differences in dielectric constants between the organic and inorganic parts, excitons in LDMHPs are spatially confined. This suppresses the separation of excitons and greatly improves the radiation recombination efficiency. Therefore, organic–inorganic LDMHPs are considered to be good candidate materials for stable LEDs with highefficiency. Most 2D perovskite electroluminescent layers can be fabricated via the one or two-step fast crystallization spin-coating method using precursors. **Table 2** shows a performance summary of LEDs based on recent 2D MHPs. However, 1D and 0D fail to be fabricated by solution method, which is the main reason for no 1D and 0D electroluminescent diodes. Therefore, unlike "structure-level" 1D nanowire/nanorod perovskites and 0D nanocrystal perovskites, 1D and 0D organic–inorganic MHPs at the molecular level have not been used in the electroluminescent layer.^[87]

In order to prepare color-adjustable LEDs, two main strategies have been tried so far. One is to rely on mixed halides,^[88] and the other is to control quantum well structures.^[89] However, ion migration and phase separation are prone to occur under light and electric fields in LED devices with mixed halide perovskites.^[90] resulting in the changes in electroluminescent color during device operation.^[91] Controlling the quantum well structure to obtain quasi-2D perovskite is another effective method to obtain the target color. The LEDs produced by this method have a very stable

ADVANCED SCIENCE

www.advancedsciencenews.com

www.advancedscience.com



Figure 13. a) Phase transition and dielectric response of 1D MPIP perovskite structural phase transition induced by temperature. Reproduced with permission.^[77] Copyright 2018, Royal Society of Chemistry. b) Structural phase transition of $[C_6H_{11}NH_3]_2CdCl_4$ at 367 K. Reproduced with permission.^[78] Copyright 2014, American Chemical Society. c) MHy₂Pbl₄ underwent three structural phase transitions and the tilt degree of octahedral Pbl₆^{4–} at each phase.^[14] d) The interval between lead iodide sheets varies with temperature.^[14] Copyright 2019, American Chemical Society. e) CIE coordinates of MHy₂Pbl₄ at different temperatures. Reproduced with permission.^[14] Copyright 2019, American Chemical Society. e) CIE coordinates



Figure 14. a) Changes of PL spectrum of stripped monolayer $(C_4H_9NH_3)_2PbI_4$ with temperature. Reproduced with permission.^[80] Copyright 2018, American Chemical Society. b) 2D perovskite (n = 2) under laser irradiation, PL redshift, and then blueshift reversible process after laser annealing. Reproduced with permission.^[81] Copyright 2018, Springer Nature. c) Temperature-dependent changes in PL intensity, highlighting changes in the relative intensity of relaxed peak. Reproduced with permission.^[81] Copyright 2018, Springer Nature. d) The broadband emission appears at low temperature in 100-oriented 2D perovskite. Reproduced with permission.^[82] Copyright 2017, Royal Society of Chemistry.

SCIENCE NEWS ______ www.advancedsciencenews.com



www.advancedscience.com



Figure 15. a) Schematic diagram of Pb–I–Pb bond under compression in $(BA)_2PbI_4$. Reproduced with permission.^[86] Copyright 2018, AmericanChemical Society. b) 1D structure distortion caused by pressure. c) The relationship between PL spectra of $C_4N_2H_{14}SnBr_4$ and pressure, and luminescence photographs at different pressure points. b,c) Reproduced with permission.^[13] Copyright 2019, American Chemical Society. d) Optical absorption spectrum of $Cs_3Bi_2I_9$ at high pressure. Reproduced with permission.^[87] Copyright 2018, Wiley-VCH.



Figure 16. a) The photomicrograph shows that the strength of PL varies with the increase of pressure. b) The compressive structural transformation of $(BA)_4AgBiBr_8$ crystals (the pink and green octahedrons represent $[AgBr_6]$ and $[BiBr_6]$ octahedrons, respectively). c) Schematic diagram of the pressure-induced luminescence mechanism of self-trapped exciton. Reprinted with permission. ^[86] Copyright 2019, Wiley-VCH.

www.advancedsciencenews.com

Table 2. Performance summary of reported LDMHPs-based LEDs.



www.advancedscience.com

Formula	Device fabrication	EQE%	Stability		
$\overline{PEA_{2}MA_{n-1}}Pb_{n}Br_{3n+1}(n=5)^{a} [99]$	Spin-coating using precursors	7.4	N/A		
$BA_2MA_{n-1}PbnI_{3n+1}(n=11)^{b}$ [100]	Spin-coating using precursors	10.4	No degradation after storage for 8 months in $\rm N_2$		
(NMA) ₂ CsPb ₂ I ₇ ^{c)} ^[101]	Spin-coating using precursors	3.7	50% after 5 h under operation		
$(EA)_2(MA)_{n-1}Pb_nBr_{3n+1}^{d}$ [102]	Spin-coating using precursors	2.6	N/A		
PA ₂ (CsPbBr3) _{n-1} PbBr4 ^{e)} [103]	Spin-coating using precursors	3.6	50% after around 30 min under operation		
(NMA) ₂ Cs _{n-1} Pb _n I _{3n+1} ^[104]	Spin-coating using precursors	7.3	The EL emission peak does not change at different bias voltages		
BA ₂ FA ₂ Pb ₃ Br ₁₀ ^[43]	Spin-coating using precursors	14.64	The EL spectra retained up to 90% and 50% after 95 and 102 min		
$BA_2(CsPbBr_3)_{n-1}PbBr_4-PEO^{[105]}$	Spin-coating using precursors	8.42	50% after around 45 min under operation		
(NMA) ₂ FAPb ₂ I ₇ ^[106]	Spin-coating using precursors	12.7	N/A		
$(TFA)_2 MA_{n-1} Pb_n Br_{3n}^{f}$ [107]	Spin-coating using precursors	N/A	No change after 2688 h in air		
$PEA_2(FAPbBr_3)_{n-1}PbBr_4(n = 3)^{[99]}$	Spin-coating using precursors	14.36	N/A		
$(BA)_2(Cs)_{n-1}[Pb_n _{3n+1}]^{[93]}$	Spin-coating using precursors	6.23	El spectral stability under operation		
BA2DMA1.6Cs2Pb3Br11.6 ^[108]	Spin-coating using precursors	2.4	High spectrum stability at high voltage		
PEA ₂ DMA _{1.2} Cs ₂ Pb ₃ Br _{11.2} ^[108]	Spin-coating using precursors	1.58	High spectrum stability at high voltage		
PEA ₂ (Rb _{0.6} Cs _{0.4}) ₂ Pb ₃ Br ₁₀ ^[109]	Spin-coating using precursors	1.35	No spectral change after 4 h annealing		
CsPbCl _{0.9} Br _{2.1} with PEABr ^[110]	Spin-coating using precursors	5.7	El spectral stability under operation		
$(PEA)_2(CH_3NH_3)_{m-1}Pb_mBr_{3m+1} (m = 3)^{[96]}$	Spin-coating using precursors	4.98	Superior stability under exposure to light and moisture		
(BIZ) ₂ Mn _{0.23} Pb _{0.77} I ₄ ^{g)} [111]	Spin-coating using precursors	0.045	Good color stability		
$PEA_2Cs_2Pb_3Br_{10}$ (with QDs) $^{[112]}$	In situ fabrication of QDs films	8.1	Over 1 h at a current density of 10 mA cm ⁻² of continuous operation		
PEA ₂ MA ₂ Pb ₃ Br ₁₀ ^[113]	Spin-coating using precursors	9.2%±1.43	N/A		
(BA) ₂ CsPb ₂ Br ₇ (single crystals) ^[114]	Spin-coating using precursors	0.7	N/A		
$(BA)_2Cs_2Pb_3Br_{10}$ (single crystals) ^[114]	Spin-coating using precursors	1.1	N/A		

^{a)} PEA, $C_6H_5C_2H_4NH_3^{+}$ ^{b)} BA, $CH_3(CH_2)_3NH_3^{+}$ ^{c)} NMA, 1-naphthylmethyl ammonium ^{d)} EA, $C_2H_5NH_3^{+}$ ^{e)} PA, $C_3H_7NH_3^{+}$ ^{f)} TFA, $C_6H_2F_3NH_3^{+}$ ^{g)} BIZ, benzimidazolium.

electroluminescence spectrum. For example, Xing et al.^[92] introduced a short ligand (*iso-pro*-pylammonium, IPA) to partially replace the long ligand (PEA) to synthesize a quasi-2D perovskites. The growth of n = 2, 3, 4 phases become dominant, thereby adjusting the crystallization of the quasi-2D perovskites. The fabricated LEDs devices reached a maximum brightness of 2480 cd m⁻² at 490 nm and showed stable sky blue emission under high operating voltage (**Figure 17**a). In addition, Tian et al.^[93] prepared a quasi-2D perovskites /poly(ethylene oxide) (PEO) composite films by blending metal halide perovskites with polymer, and used it as a light-emitting layer to prepare a good spectral stability bright red perovskite LEDs (Figure 17b).

However, the insulating properties of the large cations limit the carrier transport in 2D perovskites, thereby reducing the radiation recombination rate of quasi-2D perovskite based LEDs.^[94] It has been reported that inorganic alkali metals with small ionic radius such as Na⁺ was used to replace large organic cations partly in perovskite layers to improve the carrier transport.^[95] Another way is to ensure the good connection of the inorganic layer through the optimized nanocrystalline pinning (NCP) process, which can effectively promote the carrier transfer in the LED devices of quasi-2D perovskites. For example, Lee et al.^[96] used the optimized NCP process to modulate the Ruddelsden– Popper (RP) phase of (PEA)₂(CH₃NH₃)_{n-1}Pb_nBr_{3n+1} nanostructure, and their RP phase units oriented randomly. This modulated nanostructure can increase the contact between adjacent quasi-2D perovskite layers, and so carriers can be effectively transported through the connection interface between the inorganic layers, greatly improving the efficiency of RP quasi-2D perovskite LEDs. When n = 3, they developed RP quasi-2D perovskite LED devices with a maximum current efficiency of 20.18 cd A⁻¹ (Figure 17c) and a maximum EQE of 4.98% (Figure 17d).

In addition, the conversion of 3D perovskites to quasi-2D perovskites will introduce more defects on the surface or grain boundaries due to the reduction of crystal size, resulting in nonradiative recombination rate, which will also reduce the electroluminescence efficiency 2D perovskite LEDs.^[97] The intrinsic defects in the perovskite films can be passivated by introducing additives, or the interface modification methods can effectively reduce the defects in the perovskite films, thereby improving the radiation recombination rate in 2D perovskite LEDs.^[98] For example, Zhao et al.^[2] reported quasi-2D and 3D (2D/3D) perovskite-polymer (poly (2-hydroxyethyl methacrylate)) heterostructure LEDs. The introduction of the polymer effectively eliminated the nonradiative recombination pathway, and the external quantum efficiency of the LED devices was as high as 20.1% (current density is 0.1-1 mA cm⁻², Figure 17e). And Yang et al.^[99] investigated LEDs with high efficiency based on quasi-2D PEA₂(FAPbBr₃)_{*n*-1}PbBr₄ (n = 3) as the emitting layer. External quantum efficiency (EQE) of the champion device with

CIENCE NEWS

sion. Great green light-emitting performance up to 97% of PLQE and excellent thermal stability made the materials an attractive candidate for white light-emitting diodes (WLEDs) manufacturing. They also fabricated WLED devices by using green-emitting crystals Cs_4PbBr_6 with $CsPbBr_3$ nanocrystals, red-emitting phosphor $K_2SiF_6:Mn^{4+}$ (KSF), and blue-emitting GaN chips. The optimized devices had a luminous efficiency of 151 lm W⁻¹ at

20 mA and a chromaticity coordinate value of (0.331, 0.331)

(Figure 18b-d). Actually, white-light-emitting from a single emitter layer is very important for solid-state lighting applications because it simplifies the device structure and avoids problems, such as selfabsorption and color instability in hybrid emitters and multiple emitters.^[46] Recently, a series of LDMHPs with 2D, 1D, and 0D structures have been reported. There is a variety of lowdimensional single crystal growth strategies including but not limited to cooling crystallization method, antisolvent method and solution method. For 2D and 1D, adjacent octahedrons can be connected by corner-sharing, edge-sharing, and face-sharing. They all exhibit broadband white-light-emitting and are applied to a single white-emitting WLED phosphor. For example, The Ma's group^[19] also reported an 1D organic halide perovskites $C_4 N_2 H_{14} PbBr_4$ with the edge-sharing octahedral lead bromide chains [PbBr42-] that emitted bluish white-light with a PLQE

Nature.

(Figure 17f).

3.2. Phosphors in Solid Lighting

trioctylphosphine oxide (TOPO) passivation layer is up to 14.36%

LDMHPs have larger exciton binding energies, which greatly in-

creases the exciton recombination rate, resulting in LDMHPs with high photoluminescence quantum yield (PLQE). The

Ma's group^[115] has reported an efficient broadband yellow-

emitting phosphors composed of 0D tin mixed halide perovskites $(C_4N_2H_{14}Br)_4SnBr_xI_{6-x}$ (x = 3). The phosphors had a full width

half maximum of 126 nm (FWHM) and a photoluminescence

quantum efficiency (PLQE) of about 85% due to the structural

reorganization of the excited state. By mixing the yellow phos-

phors and commercial Eu-doped barium magnesium aluminate blue phosphors (BaMgAl₁₀O₁₇: Eu²⁺) with the weight ra-

tio 1:4, a near-perfect white emission with CIE coordinates of

(0.32, 0.32), the color rendering index (CRI) of 84 and the cor-

related color temperature (CCT) value of 6160 K can be fabricated (Figure 18a). UV-pumped white LEDs was as high as 85.

Zhong's group^[116] used the HBr-assisted slow cooling method

(SCM) to grow centimeter-sized Cs₄PbBr₆ crystals with embed-

ded CsPbBr₃ nanocrystals, showing excellent green PL emis-



Figure 17. a) EL spectra of LEDs operating under different voltage. Inset is a photograph of the device. Reproduced with permission. ^[92] Copyright 2018, Springer Nature. b) EL spectral stability under 3.5 V continuous voltage operation. Inset is a photograph of the device. Reproduced with permission.^[93] Copyright 2018, Wiley-VCH. c) Current efficiency–voltage curve of the LED device. d) External quantum efficiency–voltage curve of the LED device. c, d) Reproduced with permission.^[96] Copyright 2019, Wiley-VCH. e) EQE-current density curve of the LEDs (peak EQE = 20.1%). Inset is the peak EQE histogram of 320 devices. Reproduced with permission.^[21] Copyright 2018, Springer Nature. f) EQE of the champion device of PEA₂(FAPbBr₃)_{*n*-1}PbBr₄ (*n* = 3 composition) with TOPO as passivation layer. Inset is the EL image of the green LED. Reproduced with permission.^[99] Copyright 2018, Springer



www.advancedsciencenews.com

ADVANCED SCIENCE

www.advancedscience.com



Figure 18. a) Emission stability and luminous performance of OD $(C_4N_2H_{14}Br)_4SnBr_xI_{6-x}$ LED. Reproduced with permission.^[115] Copyright 2017, American Chemical Society. b) Schematic diagram of the configuration of the prototype device. c) A picture of surface mounted device (left) and the WLED operated at a forward bias current (right). d) EL spectrum of the prototype WLED device. b-d) Reproduced with permission.^[116] Copyright 2018, Wiley-VCH. e) CIE coordinates of (EDBE) (PbBr₄) and sunlight at noon. Inset is a photograph of (EDBE) (PbBr₄) under 365 nm irradiation. Reproduced with permission.^[17] Copyright 2014, American Chemical Society. f) CIE coordinates and emission spectrum of white-light emitters and sunlight a noon. Inset is a photograph of (N-MEDA)[PbBr₄] under 380 nm irradiation. Reproduced with permission.^[46] Copyright 2014, American Chemical Society. g) CIE coordinate of (EDBE)PbBr₄. Inset is an image of a UV-pumped WLED. Reproduced with permission.^[124] Copyright 2016, Wiley-VCH.

Dimension ^{a)}	Formula	Connecting type	Fabrication	Peak [nm]	FWHM [nm]	PLQE [%]
21-110-2D ^[45]	α-(DMEN)PbBr ₄	Corner-sharing	Cooling crystallization	≈520	≈180	N/A
22-110-2D ^[46]	(<i>N</i> -MEDA)[PbBr _{4-x} Cl _x]	Corner-sharing	Solution method	≈530	220	<1.5
23-110-2D ^[47]	C ₆ H ₁₃ C _{I4} N ₃ Pb	Corner-sharing	Solution evaporation	573	220	<1
25-110-2D ^[25]	(PDA) ₇ Pb ₆ Br ₂₆	Corner-sharing	Antisolvent method	671	265	6.7
27-110-2D ^[17]	(EDBE)[PbBr ₄]	Corner-sharing	Solution method	573	215	9
27-100-2D ^[17]	(EDBE)[PbCl ₄]	Corner-sharing	Solution method	538	208	2
20-100-2D ^[10]	(CH ₃ CH ₂ NH ₃) ₄ Pb ₃ Br _{10-x} Cl _x	Corner-sharing	Solution method	359-450	150–228	N/A
24-100-2D ^[48]	(2meptH ₂)PbBr ₄	Corner-sharing	Solution method	417	≈50	3.37
18-1D ^[12]	$(C_3N_3H_{10}O)(C_3N_3H_{11}O)_2Pb_2Br_9$	Corner-sharing	Antisolvent method	530	218	1.7
25-1D ^[25]	(EDA) ₂ PbBr ₆	Corner-sharing	Antisolvent method	523	138	9.1
17-0D ^[121]	(C ₄ N ₂ H ₁₄ I) ₄ SnI ₆	N/A	Antisolvent method	620	188	75 <u>+</u> 4
17-0D ^[121]	(C ₄ N ₂ H ₁₄ Br) ₄ SnBr ₆	N/A	Antisolvent method	570	105	95±5
6-0D ^[12]	(C ₃ N ₃ H ₁₁ O) ₂ PbBr ₆ ·4H ₂ O	N/A	Antisolvent method	568	218	9.6

Table 3. Summary of reported LDMHPs phosphors used in white LED devices.

^{a)} The figures highlighted in blue refers to the corresponding organic cations shown in Figure 4.

CIENCE NEWS



www.advancedscience.com



Figure 19. a) Temperature dependence of the light yields. The inset shows details of the curves from 290 to 310 K. Reproduced with permission.^[123] Copyright 2016, Spring Nature. b) Schematic diagram of X-ray imaging setup using 1:1 Li-(PEA)₂ PbBr₄ as scintillator. c) X-ray image of the safety pin using Li-(PEA)₂ PbBr₄ as scintillator. b, c) Reproduced with permission.^[126] Copyright 2020, Spring Nature. d) Photographs of a capsule containing a spring inside, a circuit board, a crab and the corresponding X-ray images by X-ray imaging. Reproduced with permission.^[127] Copyright 2020, American Chemical Society. e) The normalized total amount of photons comparison with the same X-ray excitation. f) X-ray fluorescence spectra under 50 kV Ag tube irradiation. Gray: NaI:TI commercial scintillator. Blue: Bmpip₂PbBr₄ pellet. Red: Bmpip₂SnBr₄ pellet. e,f) Reproduced with permission.^[129] Copyright 2019, American Chemical Society. g) Schematic diagram of a simplified device for gas sensing application. h) Digital photos of (C₉NH₂₀)₂MnBr4 upon exposure to six kinds of organic vapors for 10 min under 365 nm UV excitation. g,h) Reproduced with permission.^[131] Copyright 2019, American Chemical Society.

of 20%. To utilize the phosphor-converted WLEDs for artificial lighting requirement, the CRI points of 95,^[117] the CCT of 5564 K,^[118] and the PLQE of 90%^[119] should be the standards. **Table 3** gives a summary of LDMHPs phosphors used in WLED devices. Karunadasa and his colleagues^[17,46] published 2D hybrid perovskites with 110-oriented broadband white-light-emitting, namely (EDBE)PbBr₄ (Figure 18e) and (*N*-MEDA)PbBr₄ (Fig-

ure 18f), which had broadband white-light-emitting due to the formation of self-trapped excitons in the deformable lattice. Recently, Ma's group^[120] reported a high-luminance micrometer-scale corrugated 2D lead bromide perovskite (EDBE)PbBr₄, its emission almost cover the entire visible spectrum, and its PLQE up to 18%. This perovskite phosphor can produce white-light-emitting under the irradiation of ultraviolet lamp. The CCT

pumped by the 365 nm UV-LED chip is 6519 K, and the CIE coordinates are (0.30, 0.42) (Figure 18g).

3.3. Scintillator and Transducer

It is generally believed that LDMHPs have higher PCEs, faster decay and larger stokes shifts compared with 3D ones.^[122] These advantages demonstrate the potential of LDMHPs for large-area and low-cost scintillator devices in the field of medical imaging, nondestructive detection, space exploration, etc. For example, Birowosuto et al.^[123] reported three X-ray scintillator characteristics of 3D MAPbI₂ and MAPbBr₂ and 2D (EDBE)PbCl₄ hybrid perovskite crystals. Comparing to 3D perovskites, 2D (EDBE)PbCl₄ has less thermal quenching due to the large exciton binding energy so that moderate light yield of 9000 photons MeV⁻¹ can be obtained even at room temperature (Figure 19a). Moreover, Masanori et al.^[124] researched 2D organicinorganic hybrid perovskite-type scintillator single crystal of $5 \times 6 \times 1 \text{ mm}^3$ of (PEA)₂PbBr₄ (PEA⁺ = C₆H₅(CH₂)₂NH₃⁺). Under 662 keV gamma-ray excitation, the crystal shows a substantial light yield of 10 000 photons MeV⁻¹, with a main decay time component of 9.4 ns. Subsequently, they further optimized the crystal and investigated scintillation properties of (PEA)₂PbBr₄ under gamma-ray and X-ray irradiations. They fabricated $17 \times 23 \times 4$ mm³ bulk sample, which shows a remarkably high light yield of 14000 photons MeV⁻¹ and very fast decay time of 11 ns under gamma-rays.^[125]

In addition, Xie et al.^[126] demonstrated Li-dopant (PEA)₂PbBr₄ crystal and explored the application of Li-(PEA)₂PbBr₄ scintillator in alpha particle detection, X-ray imaging and discrimination between alpha particle and gamma-ray. It is worth mentioning that they obtained first satisfactory X-ray imaging pictures of a ubiquitous safety pin using Li-(PEA)₂PbBr₄ film (Figure 19b,c). However, the toxicity of lead in these lead-based halide perovskites may restrict its potential commercial applications. Thereby, Cao and his colleagues^[127] developed a lead-free 2D layered (C₈H₁₇NH₃)₂SnBr₄ perovskite scintillators, which not only exhibit a high PCE of 98% and a large Stokes shift of 246 nm but also provide nontoxicity, good PL intensity, and stability under X-ray illumination. The results make the novel perovskite scintillators suitable for X-ray imaging applications (Figure 19d). And Hardhienata et al.^[128] studied the optical and scintillation properties of manganese-based 2D organic-inorganic hybrid perovskite crystals X_2 MnCl₄ (X = PEA, PPA). Both of them show promising PL properties, reasonable decay time (about 3-4 µs) and small bandgaps (about 2 eV), making them applicable for scintillator in X-ray imaging application. Viktoriia et al.[129] reported isostructural 0D halide complexes of Bmpip₂SnBr₄ and $Bmpip_2PbBr_4$ (Bmpip = 1-butyl-1-methylpiperidinium cation) that can exhibit potent X-ray fluorophores being comparable to that of a commercial inorganic NaI:T1 X-ray scintillator (Figure 19e,f).

At the same time, LDMHPs have also shown potential in transducer field due to their adjustable structural phase transition and fluorescence emissions. For example, Zhou and his colleague^[130] reported a novel 0D all-inorganic perovskite single crystal $Cs_2InBr_5 \cdot H_2O$ for sensitive water detection. And Li et al.^[131] have carefully researched the temperature-dependent phase transition www.advancedscience.com

and photoluminescence properties of 0D organic–inorganic hybrid metal halide $(C_9NH_{20})_2MnBr_4$. Based on this compound, they further developed a fluorescent sensor for Acetone. By simplified gas-sensitive detecting device with $(C_9NH_{20})_2MnBr_4$, rapid fluorescence quenching shows when the organic solvent is acetone, which cannot be found when applying other organic solvents (Figure 19g,h).

4. Prospects and Outlook

As a new perovskite-type photovoltaic material system, LDMHPs exhibit excellent stability to water, heat and light, and are expected to solve the instability problem of traditional 3D perovskites, which plays a crucial role for the final industrialization of perovskite materials. By adjusting the dimensions and crystal structures, LDMHPs are expected to provide more opportunity for various optoelectronic devices. However, the LDMHP are still a new type material which has not been fully developed yet, and there are still some problems to be solved

- a) How to decrease environmental pollution. Although the stability of organic–inorganic hybrid perovskites has been greatly improved, the potential toxicity problem of Pb²⁺ has not been solved. At present, some people try to use other metal elements to replace or partially replace Pb to prepare lead-free or lead-less perovskite solar cells, however, the PCE is not ideal. Public health concerns about lead toxicity will promote the development of lead-free LDMHPs.
- b) Currently, LDMHPs with inherent white emission have many attractive advantages, but their PLQEs are still too low when used in WLEDs. Moreover, there is a lack of systematic researches and understanding of the design, synthesis, and luminescence process mechanism of these LDMHPs. In addition, 1D and 0D perovskite materials still need a lot of work to explore especially for the application to LED devices.
- c) Although more and more LDMHPs-based optoelectronic devices show multifunctional performance and long-term stability, the properties of intrinsic materials and the composite dynamic process need further research. At the same time, an in-depth understanding of the structure-performance relationship is very necessary for the continued development of LDMHPs.

Acknowledgements

This work was supported by funding from the National Natural Science Foundation (Nos. 21703008 and 22075022) and the "Cultivate Creative Talents Project" of Beijing Institute of Technology (BIT).

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Y.H. and S.Y. contributed equally to this work. All the authors contibuted to the discussion of the content, writing and editing of manuscript prior to submission.

www.advancedsciencenews.com

Keywords

light emitting diodes, low-dimensional perovskites, luminescence, phosphors, structure regulation

- Received: December 15, 2020
- Revised: April 18, 2021
- Published online: June 17, 2021
- a) H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang, *Science* **2014**, *345*, 542; b) A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050; c) J. Chen, X. Cai, D. Yang, D. Song, J. Wang, J. Jiang, A. Ma, S. Lv, M. Z. Hu, C. Ni, *J. Power Sources* **2017**, *355*, 98.
- [2] B. Zhao, S. Bai, V. Kim, R. Lamboll, R. Shivanna, F. Auras, J. M. Richter, L. Yang, L. Dai, M. Alsari, *Nat. Photonics* 2018, 12, 783.
- [3] C. C. Stoumpos, M. G. Kanatzidis, Adv. Mater. 2016, 28, 5778.
- [4] J. J. Yoo, G. Seo, M. R. Chua, T. G. Park, Y. Lu, F. Rotermund, Y.-K. Kim, C. S. Moon, N. J. Jeon, J.-P. Correa-Baena, *Nature* **2021**, *590*, 587.
- [5] S. Sun, T. Salim, N. Mathews, M. Duchamp, C. Boothroyd, G. Xing, T. C. Sum, Y. M. Lam, *Energy Environ. Sci.* 2014, *7*, 399.
- [6] R. K. Misra, B.-E. Cohen, L. lagher, L. Etgar, ChemSusChem 2017, 10, 3712.
- [7] L. Mao, C. C. Stoumpos, M. G. Kanatzidis, J. Am. Chem. Soc. 2019, 141, 1171.
- [8] Z. Xiao, W. Meng, J. Wang, D. B. Mitzi, Y. Yan, Mater. Horiz. 2017, 4, 206.
- [9] K. I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, Y. Tokura, *Nature* 1998, 395, 677.
- [10] L. Mao, Y. Wu, C. C. Stoumpos, B. Traore, C. Katan, J. Even, M. R. Wasielewski, M. G. Kanatzidis, J. Am. Chem. Soc. 2017, 139, 11956.
- [11] J. Yin, H. Yang, K. Song, A. M. El-Zohry, Y. Han, O. M. Bakr, J.-L. Brédas, O. F. Mohammed, J. Phys. Chem. Lett. 2018, 9, 5490.
- [12] B.-B. Cui, Y. Han, B. Huang, Y. Zhao, X. Wu, L. Liu, G. Cao, Q. Du, N. Liu, W. Zou, *Nat. Commun.* **2019**, *10*, 1.
- [13] Y. Shi, Z. Ma, D. Zhao, Y. Chen, Y. Cao, K. Wang, G. Xiao, B. Zou, J. Am. Chem. Soc. 2019, 141, 6504.
- [14] M. Mączka, M. Ptak, A. Gągor, D. Stefańska, A. Sieradzki, Chem. Mater. 2019, 31, 8563.
- [15] P. Chen, Y. Bai, M. Lyu, J. H. Yun, M. Hao, L. Wang, Sol. RRL 2018, 2, 1700186.
- [16] J. Yin, H. Li, D. Cortecchia, C. Soci, J.-L. Brédas, ACS Energy Lett. 2017, 2, 417.
- [17] E. R. Dohner, A. Jaffe, L. R. Bradshaw, H. I. Karunadasa, J. Am. Chem. Soc. 2014, 136, 13154.
- [18] Mitzi, D. B., J. Chem. Soc. Dalton Trans. 2001, 1, 1.
- [19] Z. Yuan, C. Zhou, Y. Tian, Y. Shu, J. Messier, J. C. Wang, L. J. van de Burgt, K. Kountouriotis, Y. Xin, E. Holt, *Nat. Commun.* **2017**, *8*, 1.
- [20] M. E. Kamminga, H. H. Fang, M. R. Filip, F. Giustino, J. Baas, G. R. Blake, M. A. Loi, T. T. M. Palstra, *Chem. Mater.* **2016**, *28*, 4554.
- [21] Romain, G., Florian, M., Gabin, G., Michael, P., Adv. Mater. 2019, 31, 1807383.
- [22] Y. Y. Pan, Y. H. Su, C. H. Hsu, L. W. Huang, C. C. Kaun, Comput. Mater. Sci. 2016, 117, 573.
- [23] C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp, M. G. Kanatzidis, *Chem. Mater.* **2016**, *28*, 2852.
- [24] A. Lemmerer, D. G. Billing, CrystEngComm 2012, 14, 1954.
- [25] Y. Han, Y. Li, Y. Wang, G. Cao, S. Yue, L. Zhang, B. B. Cui, Q. Chen, *Adv. Opt. Mater.* 2020, *8*, 1902051.
- [26] C. Zhou, Y. Tian, O. Khabou, M. Worku, Y. Zhou, J. Hurley, H. Lin, B. Ma, ACS Appl. Mater. Interfaces 2017, 9, 40446.



www.advancedscience.com

- [27] G. Wu, C. Zhou, W. Ming, D. Han, S. Chen, D. Yang, T. Besara, J. Neu, T. Siegrist, M.-H. Du, B. Ma, A. Dong, ACS Energy Lett. 2018, 3, 1443.
- [28] C. Zhou, T. Yu, M. Wang, A. Rose, B. Ma, Angew. Chem., Int. Ed. 2017, 56, 9018.
- [29] C. Zhou, H. Lin, Y. Tian, Z. Yuan, R. Clark, B. Chen, L. J. van de Burgt, J. C. Wang, Y. Zhou, K. Hanson, *Chem. Sci.* **2018**, *9*, 586.
- [30] C. Zhou, M. Worku, J. Neu, H. Lin, Y. Tian, S. Lee, Y. Zhou, D. Han, S. Chen, A. Hao, *Chem. Mater.* 2018, 30, 2374.
- [31] C. Zhou, H. Lin, M. Worku, J. Neu, Y. Zhou, Y. Tian, S. Lee, P. Djurovich, T. Siegrist, B. Ma, J. Am. Chem. Soc. 2018, 140, 13181.
- [32] C. Zhou, H. Lin, H. Shi, Y. Tian, C. Pak, M. Shatruk, Y. Zhou, P. Djurovich, M. H. Du, B. Ma, Angew. Chem., Int. Ed. 2018, 130, 1033.
- [33] Y. Takeoka, K. Asai, M. Rikukawa, K. Sanui, *Chem. Lett.* **2005**, *34*, 602.
- [34] H. Lin, C. Zhou, M. Chaaban, L. J. Xu, B. Ma, ACS Mater. Lett. 2019, 1, 594.
- [35] G. Song, M. Li, Y. Yang, F. Liang, Z. Lin, J. Phys. Chem. Lett. 2020, 12, 86.
- [36] A. Biswas, R. Bakthavatsalam, S. R. Shaikh, A. Shinde, A. Lohar, S. Jena, R. G. Gonnade, J. Kundu, *Chem. Mater.* 2019, *31*, 2253.
- [37] W. Zhang, K. Tao, C. Ji, Z. Sun, J. Luo, Inorg. Chem. 2018, 57, 4239.
- [38] C. Xue, Z.-Y. Yao, J. Zhang, W.-L. Liu, J.-L. Liu, X.-M. Ren, Chem. Commun. 2018, 54, 4321.
- [39] H. Lin, C. Zhou, Y. Tian, T. Besara, J. Neu, T. Siegrist, Y. Zhou, J. Bullock, K. S. Schanze, W. Ming, *Chem. Sci.* 2017, *8*, 8400.
- [40] Y. Peng, Y. Yao, L. Li, Z. Wu, S. Wang, J. Luo, J. Mater. Chem. C 2018, 6, 6033.
- [41] A. Zeb, Z. Sun, A. Khan, S. Zhang, T. Khan, M. A. Asghar, J. Luo, Inorg. Chem. Front. 2018, 5, 897.
- [42] S. Lee, D. B. Kim, I. Hamilton, M. Daboczi, Y. S. Nam, B. R. Lee, B. Zhao, C. H. Jang, R. H. Friend, J. S. Kim, *Adv. Sci.* **2018**, *5*, 1801350.
- [43] G.-E. Wang, M.-S. Wang, X.-M. Jiang, Z.-F. Liu, R.-G. Lin, L.-Z. Cai, G.-C. Guo, J.-S. Huang, *Inorg. Chem. Commun.* 2011, 14, 1957.
- [44] M. Tathavadekar, S. Krishnamurthy, A. Banerjee, S. Nagane, Y. Gawli, A. Suryawanshi, S. Bhat, D. Puthusseri, A. D. Mohite, S. Ogale, J. Mater. Chem. A 2017, 5, 18634.
- [45] L. Mao, Y. Wu, C. C. Stoumpos, M. R. Wasielewski, M. G. Kanatzidis, J. Am. Chem. Soc. 2017, 139, 5210.
- [46] E. R. Dohner, E. T. Hoke, H. I. Karunadasa, J. Am. Chem. Soc. 2014, 136, 1718.
- [47] Z. Wu, C. Ji, Z. Sun, S. Wang, S. Zhao, W. Zhang, L. Li, J. Luo, J. Mater. Chem. C 2018, 6, 1171.
- [48] S. Wang, Y. Yao, J. Kong, S. Zhao, Z. Sun, Z. Wu, L. Li, J. Luo, Chem. Commun. 2018, 54, 4053.
- [49] F. Hao, C. C. Stoumpos, D. H. Cao, R. P. H. Chang, M. G. Kanatzidis, *Nat. Photonics* **2014**, *8*, 489.
- [50] S. Nancy, C. Rayan, G. Prasenjit, N. Angshuman, Chem. Asian J. 2018, 13, 2085.
- [51] J. K. Pious, M. Lekshmi, C. Muthu, R. Rakhi, V. C. Nair, ACS Omega 2017, 2, 5798.
- [52] J. Ming-Gang, D. Jun, M. Liang, Z. Yuanyuan, Z. X. Cheng, J. Am. Chem. Soc. 2018, 140, 10456.
- [53] R. Zhang, X. Mao, Y. Yang, S. Yang, W. Zhao, T. Wumaier, D. Wei, W. Deng, K. Han, Angew. Chem. Int. Ed. 2019, 58, 2725.
- [54] D. Cortecchia, H. A. Dewi, J. Yin, A. Bruno, N. Mathews, Chin. Sci. Bull. 2016, 55, 3105.
- [55] H. Liu, X. Wang, W. Hu, L. Guo, S. Ouyang, Chem. J. Internet 2004, 6, 39.
- [56] R. D. Willett, C. Galeriu, C. P. Landee, M. M. Turnbull, B. Twamley, Inorg. Chem. 2004, 43, 3804.
- [57] E. Suprayoga, A. A. Nugroho, A. O. Polyakov, T. T. M. Palstra, I. Watanabe, J. Phys. 2014, 551, 012054.
- [58] L. Guo, Y. Dai, M. Hu, H. Liu, S. Ouyang, Mater. Chem. Phys. 2011, 848, 322.

www.advancedsciencenews.com

- [59] Y. Abid, M. Kamoun, A. Daoud, F. Romain, Adv. Mat. Res. 1994, 1, 309.
- [60] W. Li, D. Zhang, T. Zhang, T. Wang, H. Li, Thermochim. Acta 1999, 326, 183.
- [61] Y. P. Lin, S. Hu, B. Xia, K. Q. Fan, L. K. Gong, J. T. Kong, X. Y. Huang, Z. Xiao, K. Z. Du, J. Phys. Chem. Lett. 2019, 10, 5219.
- [62] A. Mehdizadeh, S. F. Akhtarianfar, S. Shojaei, J. Phys. Chem. C 2019, 123, 6725.
- [63] A. Yangui, S. Pillet, A. Lusson, E. E. Bendeif, S. Triki, Y. Abid, K. Boukheddaden, J. Alloys Compd. 2017, 699, 1122.
- [64] a) A. M. Ganose, C. N. Savory, D. O. Scanlon, J. Mater. Chem. A 2017, 5, 7845; b) Z. Xiao, W. Meng, J. Wang, Y. Yan, Phys. Chem. Chem. Phys. 2016, 18, 25786.
- [65] Z. Xiao, W. Meng, B. Saparov, H. S. Duan, Y. Yan, J. Phys. Chem. Lett. 2016, 7, 1213.
- [66] Lingling, M., Peijun, G., Mika?l, K., Ido, H., Claudine, K., J. Am. Chem. Soc. 2018, 140, 13078.
- [67] Y. Li, G. Zheng, C. Lin, J. Lin, Solid State Sci. 2007, 9, 855.
- [68] H. A. Evans, D. H. Fabini, J. L. Andrews, M. Koerner, M. B. Preefer, G. Wu, F. Wudl, A. K. Cheetham, R. Seshadri, *Inorg. Chem.* 2018, 57, 10375.
- [69] X. Zhang, B. Xu, J. Zhang, Y. Gao, Y. Zheng, K. Wang, X. W. Sun, Adv. Funct. Mater. 2016, 26, 4595.
- [70] J. H. Cha, J. H. Han, W. Yin, C. Park, D. Y. Jung, J. Phys. Chem. Lett. 2017, 8, 565.
- [71] C. C. Stoumpos, L. Mao, C. D. Malliakas, M. G. Kanatzidis, *Inorg. Chem.* 2017, 56, 56.
- [72] M. E. Kamminga, G. A. De Wijs, R. W. Havenith, G. R. Blake, T. T. Palstra, *Inorg. Chem.* **2017**, *56*, 8408.
- [73] G. Song, M. Li, S. Zhang, N. Wang, P. Gong, Z. Xia, Z. Lin, Adv. Funct. Mater. 2020, 30, 2002468.
- [74] F. Li, X. Deng, F. Qi, Z. Li, D. Liu, D. Shen, M. Qin, S. Wu, F. Lin, S.-H. Jang, J. Am. Chem. Soc. 2020, 142, 20134.
- [75] M. C. Gélvez-Rueda, E. M. Hutter, D. H. Cao, N. Renaud, F. C. Grozema, J. Phys. Chem. C 2017, 121, 26566.
- [76] C.-H. Lee, N. D. Orloff, T. Birol, Y. Zhu, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J. A. Mundy, L. F. Kourkoutis, *Nature* 2013, 502, 532.
- [77] A. Zeb, Z. Sun, A. Khan, S. Zhang, J. Luo, Inorg. Chem. Front. 2018, 5, 897.
- [78] W. Q. Liao, H. Y. Ye, D. W. Fu, P. F. Li, L. Z. Chen, Y. Zhang, Inorg. Chem. 2014, 53, 11146.
- [79] E. Amerling, S. Baniya, E. Lafalce, C. Zhang, Z. V. Vardeny, L. Whittaker-Brooks, J. Phys. Chem. Lett. 2017, 8, 4557.
- [80] T. Sheikh, A. Shinde, S. Mahamuni, A. Nag, ACS Energy Lett. 2018, 3, 2940.
- [81] K. Leng, I. Abdelwahab, I. Verzhbitskiy, M. Telychko, L. Chu, W. Fu, X. Chi, N. Guo, Z. Chen, Z. Chen, *Nat. Mater.* 2018, 17, 908.
- [82] M. D. Smith, A. Jaffe, E. R. Dohner, A. M. Lindenberg, H. I. Karunadasa, *Chem. Sci.* **2017**, *8*, 4497.
- [83] L. Gang, G. Jue, K. Lingping, R. D. Schaller, H. Qingyang, L. Zhenxian, Y. Shuai, Y. Wenge, S. C. C., K. M. G., *Proc. Natl. Acad. Sci. USA* 2018, 115, 8076.
- [84] M. D. Smith, B. A. Connor, H. I. Karunadasa, Chem. Rev. 2019, 119, 3104.
- [85] Z. Long, L. Chunming, W. Lingrui, L. Cailong, W. Kai, Z. Bo, J. Am. Chem. Soc. 2018, 141, 1235.
- [86] T. Yin, B. Liu, J. Yan, Y. Fang, M. Chen, W. K. Chong, S. Jiang, J.-L. Kuo, J. Fang, P. Liang, J. Am. Chem. Soc. 2018, 141, 1235.
- [87] Z. Long, L. Chunming, W. Lingrui, L. Cailong, W. Kai, Z. Bo, Angew. Chem. Int. Ed. 2018, 57, 11213.
- [88] A. Dutta, R. K. Behera, P. Pal, S. Baitalik, N. Pradhan, Angew. Chem., Int. Ed. 2019, 131, 5608.

- [89] J. C. Blancon, H. Tsai, W. Nie, C. C. Stoumpos, L. Pedesseau, C. Katan, M. Kepenekian, C. M. M. Soe, K. Appavoo, M. Y. Sfeir, *Science* 2017, 355, 1288.
- [90] a) E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, M. D. McGehee, *Chem. Sci.* 2015, 6, 613; b) G. Li, F. W. R. Rivarola, N. J. L. K. Davis, S. Bai, T. C. Jellicoe, D. L. P. Francisco, S. Hou, C. Ducati, F. Gao, R. H. Friend, *Adv. Mater.* 2016, *28*, 3528.
- [91] P. Vashishtha, J. E. Halpert, Chem. Mater. 2017, 29, 5965.
- [92] J. Xing, Y. Zhao, M. Askerka, L. N. Quan, X. Gong, W. Zhao, J. Zhao, H. Tan, G. Long, L. Gao, *Nat. Commun.* **2018**, *9*, 1.
- [93] Y. Tian, C. Zhou, M. Worku, X. Wang, Y. Ling, H. Gao, Y. Zhou, Y. Miao, J. Guan, B. Ma, Adv. Mater. 2018, 30, 1707093.
- [94] H. Tsai, W. Nie, J.-C. Blancon, C. C. Stoumpos, R. Asadpour, B. Harutyunyan, A. J. Neukirch, R. Verduzco, J. J. Crochet, S. Tretiak, *Nature* 2016, 536, 312.
- [95] C. Li, A. Wang, L. Xie, X. Deng, K. Liao, J.-a. Yang, T. Li, F. Hao, J. Mater. Chem. A 2019, 7, 24150.
- [96] H. D. Lee, H. Kim, H. Cho, W. Cha, Y. Hong, Y. H. Kim, A. Sadhanala, V. Venugopalan, J. S. Kim, J. W. Choi, *Adv. Funct. Mater.* **2019**, *29*, 1901225.
- [97] X. Yang, X. Zhang, J. Deng, Z. Chu, Q. Jiang, J. Meng, P. Wang, L. Zhang, Z. Yin, J. You, Nat. Commun. 2018, 9, 1.
- [98] Y. Zou, Z. Yuan, S. Bai, F. Gao, B. Sun, Mater. Today Nano 2019, 5, 100028.
- [99] L. N. Quan, Y. Zhao, F. P. García de Arquer, R. Sabatini, G. Walters, O. Voznyy, R. Comin, Y. Li, J. Z. Fan, H. Tan, *Nano Lett.* **2017**, *17*, 3701.
- [100] Z. Xiao, R. A. Kerner, L. Zhao, N. L. Tran, K. M. Lee, T.-W. Koh, G. D. Scholes, B. P. Rand, *Nat. Photonics* 2017, *11*, 108.
- [101] S. Zhang, C. Yi, N. Wang, Y. Sun, W. Zou, Y. Wei, Y. Cao, Y. Miao, R. Li, Y. Yin, Adv. Mater. 2017, 29, 1606600.
- [102] Q. Wang, J. Ren, X.-F. Peng, X.-X. Ji, X.-H. Yang, ACS Appl. Mater. Interfaces 2017, 9, 29901.
- [103] P. Chen, Y. Meng, M. Ahmadi, Q. Peng, C. Gao, L. Xu, M. Shao, Z. Xiong, B. Hu, *Nano Energy* **2018**, *50*, 615.
- [104] J. Chang, S. Zhang, N. Wang, Y. Sun, Y. Wei, R. Li, C. Yi, J. Wang, W. Huang, J. Phys. Chem. Lett. 2018, 9, 881.
- [105] Z. Wang, F. Wang, W. Sun, R. Ni, S. Hu, J. Liu, B. Zhang, A. Alsaed, T. Hayat, Z. a. Tan, Adv. Funct. Mater. 2018, 28, 1804187.
- [106] W. Zou, R. Li, S. Zhang, Y. Liu, N. Wang, Y. Cao, Y. Miao, M. Xu, Q. Guo, D. Di, *Nat. Commun.* **2018**, *9*, 1.
- [107] J. Guo, Z. J. Shi, Y. D. Xia, W. Qi, Y. H. Chen, G. C. Xing, H. Wei, Opt. Express 2018, 26, A66.
- [108] S. Zeng, S. Shi, S. Wang, Y. Xiao, J. Mater. Chem. C 2020, 8, 1319.
- [109] Y. Cui, H. Yao, J. Zhang, T. Zhang, Y. Wang, L. Hong, K. Xian, B. Xu, S. Zhang, J. Peng, *Nat. Commun.* **2019**, *10*, 1.
- [110] Z. Li, Ziming, C., Yongchao, Y., Qifan, X., Hin-Lap, Y., Nat. Commun. 2019, 10, 1.
- [111] L. Zhang, T. Jiang, C. Yi, J. Wu, X.-K. Liu, Y. He, Y. Miao, Y. Zhang, H. Zhang, X. Xie, J. Phys. Chem. Lett. 2019, 10, 3171.
- [112] Y. Wang, X. Bai, T. Wang, L. Yan, T. Zhang, Y. Zhang, W. Y. William, *Nanotechnology* **2017**, *28*, 215703.
- [113] H. Tsai, C. Liu, E. Kinigstein, M. Li, S. Tretiak, M. Cotlet, X. Ma, X. Zhang, W. Nie, Adv. Sci. 2020, 7, 1903202.
- [114] H. Chen, J. Lin, J. Kang, Q. Kong, D. Lu, J. Kang, M. Lai, L. N. Quan, Z. Lin, J. Jin, *Sci. Adv.* **2020**, *6*, eaay4045.
- [115] C. Zhou, Y. Tian, Z. Yuan, H. Lin, B. Chen, R. Clark, T. Dilbeck, Y. Zhou, J. Hurley, J. Neu, ACS Appl. Mater. Interfaces 2017, 9, 44579.
- [116] X. Chen, F. Zhang, Y. Ge, L. Shi, S. Huang, J. Tang, Z. Lv, L. Zhang, B. Zou, H. Zhong, *Adv. Funct. Mater.* 2018, 28, 1706567.
- [117] Y. N. Ahn, K. Do Kim, G. Anoop, G. S. Kim, J. S. Yoo, Sci. Rep. 2019, 9, 1.
- [118] C.-C. Huang, T.-H. Weng, C.-L. Lin, Y.-K. Su, Coatings 2021, 11, 239.
- [119] G.-E. Wang, G. Xu, M.-S. Wang, L.-Z. Cai, W.-H. Li, G.-C. Guo, *Chem. Sci.* 2015, 6, 7222.



www.advancedscience.com





www.advancedscience.com

- [120] D. Cortecchia, S. Neutzner, A. R. Srimath Kandada, E. Mosconi, D. Meggiolaro, F. De Angelis, C. Soci, A. Petrozza, J. Am. Chem. Soc. 2017, 139, 39.
- [121] C. Zhou, H. Lin, Y. Tian, Z. Yuan, R. Clark, B. Chen, J. Neu, T. Besara, T. Siegrist, E. Lambers, P. Djurovich, B. Ma, *Chem. Sci.* 2018, *9*, 586.
- [122] a) M. Bokdam, T. Sander, A. Stroppa, S. Picozzi, D. Sarma, C. Franchini, G. Kresse, *Sci. Rep.* **2016**, *6*, 28618; b) J.-C. Blancon, A. V. Stier, H. Tsai, W. Nie, C. C. Stoumpos, B. Traore, L. Pedesseau, M. Kepenekian, F. Katsutani, G. Noe, *Nat. Commun.* **2018**, *9*, 2254.
- [123] M. Birowosuto, D. Cortecchia, W. Drozdowski, K. Brylew, W. Lachmanski, A. Bruno, C. Soci, *Sci. Rep.* 2016, 6, 1.
- [124] Z. Yuan, C. Zhou, J. Messier, Y. Tian, Y. Shu, J. Wang, Y. Xin, B. Ma, Adv. Opt. Mater. 2016, 4, 2009.
- [125] N. Kawano, M. Koshimizu, G. Okada, Y. Fujimoto, N. Kawaguchi, T. Yanagida, K. Asai, *Sci. Rep.* 2017, *7*, 1.

- [126] A. Xie, C. Hettiarachchi, F. Maddalena, M. E. Witkowski, M. Makowski, W. Drozdowski, A. Arramel, A. T. Wee, S. V. Springham, P. Q. Vuong, *Commun. Mater.* **2020**, *1*, 37.
- [127] J. Cao, Z. Guo, S. Zhu, Y. Fu, H. Zhang, Q. Wang, Z. Gu, ACS Appl. Mater. Interfaces 2020, 12, 19797.
- H. Hardhienata, F. Ahmad, M. Aminah, D. Onggo, L. J. Diguna, M.
 D. Birowosuto, M. E. Witkowski, M. Makowski, W. Drozdowski, J. Phys. D: Appl. Phys. 2020, 53, 455303.
- [129] V. Morad, Y. Shynkarenko, S. Yakunin, A. Brumberg, R. D. Schaller, M. V. Kovalenko, J. Am. Chem. Soc. 2019, 141, 9764.
- [130] L. Zhou, J. F. Liao, Z. G. Huang, J. H. Wei, X. D. Wang, W. G. Li, H. Y. Chen, D. B. Kuang, C. Y. Su, Angew. Chem., Int. Ed. 2019, 58, 5277.
- [131] M. Li, J. Zhou, M. S. Molokeev, X. Jiang, Z. Lin, J. Zhao, Z. Xia, *Inorg. Chem.* 2019, 58, 13464.



Ying Han was born in Hebei province, China, in 1994. She joined BIT in 9/2019 as a Ph.D. candidate in School of Chemistry and Chemical Engineering and Advanced Research Institute of Multidisciplinary Science (ARIMS). She is devoted to the single crystal growth, structure regulation, luminescence mechanism, and applications of low-dimensional metal halide perovskites.



Sijia Yue was born in Anhui province, China, in 1995. She graduated from Anhui University and earned her B.E. degree in 2018. Then, she joined the group of Professor Cui in ARIMS of BIT as a postgraduate. Her research interests include the synthesis of low-dimensional perovskite single crystals and their applications in the field of optoelectronics.



Bin-Bin Cui obtained his Ph.D. degree in Institute of Chemistry, Chinese Academy of Sciences (CAS), and University of CAS in 2016. He has been a visiting scholar in Nanyang Technological University (NTU, 2015–2016) and later he joined Beijing Institute of Technology (BIT) as an associate professor. His research interests are to explore the chemical properties and applications of organic–inorganic hybrid photoelectric functional materials including perovskite photovoltaic devices, hole transporting materials for perovskite solar cells and low-dimensional perovskite crystals for luminescence.