



Article Metal Halide Perovskite Single Crystals: From Growth Process to Application

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Abstract: As a strong competitor in the field of optoelectronic applications, organic-inorganic metal hybrid perovskites have been paid much attention because of their superior characteristics, which include broad absorption from visible to near-infrared region, tunable optical and electronic properties, high charge mobility, long exciton diffusion length and carrier recombination lifetime, etc. It is noted that perovskite single crystals show remarkably low trap-state densities and long carrier diffusion lengths, which are even comparable with the best photovoltaic-quality silicon, and thus are expected to provide better optoelectronic performance. This paper reviews the recent development of crystal growth in single-, mixed-organic-cation and fully inorganic halide perovskite single crystals, in particular the solution approach. Furthermore, the application of metal hybrid perovskite single crystals and future perspectives are also highlighted.

Keywords: perovskite single crystals; growth process; application; solar cell; photodetector

1. Introduction

Recently, organic-inorganic metal hybrid perovskites have shown great applied potential because of their impressive optical and electrical properties [1–5], which can be represented by the structure ABX₃, where A is CH₃NH₃⁺, CH(NH₂)₂⁺ or Cs⁺, B is Pb²⁺ or Sn²⁺, and X is I⁻, Br⁻ or Cl⁻ [6–27]. The ideal ABX₃ structure is cubic symmetry, where A and B ions are located at the eight corners and center of a cubic unit, respectively. The symmetry of ABX₃ structures is based on the atomic species of the A and B sites. In a typical perovskite crystal structure, the A, B, and X ionic radii, e.g., R_A, R_B, and R_X , should correspond to a specific geometric relationship, known as the Tolerance factor [28–30]: $t = (R_A + R_X)/\sqrt{2(R_B + R_X)}$. The ideal value of t should be 1 for cubic structures; otherwise, the structure tends to be distorted, or even destroyed [28,30,31]. For lead hybrid perovskite, the large organic cation at the A position, e.g., methylammonium (MA⁺) or formamidinium (FA⁺), is able to match the large radius of the Pb^{2+} ion at the B position and meet the tolerance factor *t*, while the halogen anions or their mixtures occupy the C positions, resulting in the formation of a 3D perovskite structure [32]. These perovskite-based materials, when used in the photovoltaic field, can provide remarkable properties, such as broad absorption from the visible to the near-infrared region, tunable optical and electronic properties [15,33–36], high charge mobility, and long exciton diffusion length and carrier recombination lifetime [32,37–48]. Within a few years, they have revolutionized the

photovoltaic field; an efficiency of 22.1% from solution-processable perovskite-based solar cells has been reported [49]. In addition, lead hybrid perovskites have also been used in some other fields, such as laser [50], photodetector [51], light-emitting-diodes [52], thermoelectricity [53], and catalysis [54], demonstrating their potential application prospects.

Until now, many intensive investigations have been based on polycrystalline thin films, one of the existing forms of perovskite, and most of the results have been focused on the perovskite polycrystalline film. With in-depth research, single crystals—another form of perovskite—have been found with low defect density. The carrier diffusion length of perovskite is sensitive to defects. When expanding the grain size, the carrier diffusion length of polycrystalline forms can increase to up to 1 µm, while large single crystals are able to provide even longer carrier diffusion lengths. Dong et al. prepared millimeter-sized MAPbI₃ single crystals via a low-temperature solution approach, in which a carrier diffusion length of over 175 μ m was obtained under 1 sun illumination, and a longer carrier diffusion length exceeding 3 mm could be produced under a weaker illumination with 0.003% sun illumination [55]. Shi et al. reported low trap-state density of states with an order of 10^9-10^{10} cm⁻³ and carrier diffusion length > 10 mm in MAPbX₃ single crystals [40]. The longer carrier diffusion length in single crystals with low trap-state density derives from their better extraction and transport of photogenerated charge carriers, resulting in a performance boost for optoelectronic devices. These meaningful findings will contribute to the development of perovskite-based materials, and will be extremely beneficial to further fundamentally investigate the intrinsic properties of perovskites single crystals. To date, single-organic-cation, mixed-organic-cation, and all-inorganic kinds of metal halide perovskite single crystals have been demonstrated. In this review, we will summarize the advances in the growth and application of the above perovskite single crystals.

2. Growth of Organic-Inorganic Hybrid Halide Perovskite Single Crystals

Since organic-inorganic metal hybrid perovskite solar cells (PSCs) were studied for the first time [5], they have attracted particular attention due to their extraordinary performance. Since then, in-depth study on perovskite-based materials and devices has been carried out, and a series of research results have been obtained. Meanwhile, perovskite single crystals, which were reported about forty years ago [40,56,57], are studied again.

2.1. Growth of Single-Organic-Cation Halide Perovskite Single Crystals

Solution temperature lowering (STL) is a traditional single crystal growth process. In 1987, Poglitsch et al. gained MA-based perovskite single crystals via a temperature-lowering method [58] in which they heated the mixed solution to 100 °C, and perovskite single crystals were grown by cooling the solution to room temperature. In general, minimizing the number of nuclei is crucial to growing large single crystals. As an improved technology, seed-assisted growth is often adopted for the purpose of growing large-sized and high-quality single crystals, i.e., small crystals are firstly put into a single crystal precursor, followed the temperature-lowering process. Using a slow cooling rate of 0.1–0.2 °C/h, Su et al. obtained large MAPbI₃ single crystals with sizes of up to 1 cm [59] by a process in which small crystals were firstly obtained by spontaneous nucleation (Figure 1a), then high-quality as-grown crystals were selected as seeds and dropped back into the mother liquid to grow large single crystals (Figure 1b). Similarly, MAPbBr₃ single crystals with perfect cubic structure were formed. Dang et al. grew tetragonal MAPbI₃ bulk single crystals with dimensions of 10 mm × 10 mm × 8 mm by a seed-assisted growth method [60] in which the seeded crystal was fixed in the middle of the solution. The solution was saturated gradually with a decrease of temperature from 65 °C to 40 °C, resulting in the formation of high-quality single crystals over the following few days.

Huang's [36] group grew large bulk MAPbI₃ single crystals with a size of 10 mm \times 3.3 mm via a temperature-lowering method, as presented in Figure 1c, in which the seed crystal was fixed in the top half of the solution. Importantly, they dissolved the seed crystals in the bottom of the precursor solution, and the super saturation of the top solution was readily induced because of the temperature

gradient between the top and bottom, leading to fast-growing of single crystals with a rate of about 2 mm per day.



Figure 1. (a) MAPbI₃ crystal grains obtained by spontaneous nucleation; and (b) grown large MAPbI₃ crystals obtained using seeds. Reprinted with permission from [59], Copyright 2015, Elsevier B.V.; (c) large bulk MAPbI₃ single crystals with sizes of 10 mm \times 3.3 mm. Reprinted with permission from [36], Copyright 2015, American Association for the Advancement of Science; (d) MAPbI₃ single crystal grown using the BSSG method. Reprinted with permission from [61], Copyright 2015, Springer; (e) CH₃NH₃SnI₃ and (f) CH(NH₂)₂SnI₃ single crystals grown via the TSSG method. Reprinted with permission from [62], Copyright 2016, Wiley; (g) NH(CH₃)₃SnCl₃ and (h) NH(CH₃)₃SnBr₃ single crystals prepared via the BSSG method. Reprinted with permission from [63], Copyright 2016, American Chemical Society; (i) MAPbI₃(Cl) bulk single crystals grown by rapid solution temperature-lowering method. Reprinted with permission from [64], Copyright 2016, American Chemical Society; (j) mixed-halide perovskite single crystals with different halide compositions. Reprinted with permission from [65], Copyright 2015, Springer.

Using the bottom-seeded solution growth (BSSG) method, Lian et al. [61] prepared centimeter-sized bulk MAPbI₃ single crystals. To eliminate the negative effect of multiple nuclei, a seed crystal was fixed by platinum wire to segregate the seed crystal from the bottom of the flask, and the desired single crystal, 12 mm \times 12 mm \times 7 mm in size, was obtained by lowering the temperature of the growth solution from 373 K to 330 K, as shown in Figure 1d.

Tin-based perovskite single crystals have also been harvested by the temperature-lowering method. Tao and co-worker reported bulk cubic $CH_3NH_3SnI_3$ and $CH(NH_2)_2SnI_3$ single crystals grown via a top-seeded solution growth (TSSG) method (Figure 1e,f) [62]. Similarly, $NH(CH_3)_3SnX_3$ (X = Cl, Br) single crystals were prepared via the TSSG method [63], as shown in Figure 1g,h.

Lian et al. reported a rapid solution temperature-lowering method to prepare Mixed-halide perovskite single crystals based on the addition of chlorine [64]. With the addition of chlorine, the surface free energy and the edge free energy were changed. The resulting edge free energy is expressed by: $\rho_{Chlorine} = \rho - k_B T \ln C_{Chlorine}$, given that the edge free energy $\rho_{Chlorine}$ decreases with $C_{Chlorine}$, the

harvested large CH3NH3PbI3(Cl) v

growth rate of CH₃NH₃PbI₃(Cl) crystal face will increase. They harvested large CH₃NH₃PbI₃(Cl) with sizes of 20 mm × 18 mm × 6 mm within only 5 days (Figure 1i) that possessed excellent properties, i.e., a high carrier mobility of $167 \pm 35 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, a low trap-state density of $7.6 \times 10^8 \text{ cm}^{-3}$, and a transient carrier lifetime as long as $449 \pm 76 \text{ }\mu\text{s}$. Mixed-halide perovskite single crystals can also be grown via solw temperature-lowering method [65]. At 100 °C, a super-saturated aqueous solution, including single or mixed haloid acid of different halide ratios, mixing methylamine and lead (II) acetate, was prepared. By gradually lowering the precursor solution temperature, a series of perovskite single crystals, depending on the different halide ratios, could readily be formed, as presented in Figure 1j. As is shown, for both MAPbBr_{3-x}Cl_x and MAPbI_{3-x}Br_x single crystals, the color varies with the different halide ratios of Br/(Cl + Br) and I/(I + Br).

The STL method provides a simple and effective approach for the growth of MAPbX₃ and FAPbX₃, in which the crystals are formed with the decrease in the temperature of the precursor solution. However, the drawback of its being highly time-consuming (typically more than two weeks to gain one-centimeter-sized crystals [61,62]) limits its extensive use. On the other hand, the solute solubility in solvents decreases with increasing temperature for a few materials [66], i.e., inverse temperature solubility, which is also present for organic-inorganic metal hybrid perovskites. For example, MAPbI₃, MAPbBr₃ and MAPbCl₃ show inverse temperature solubility in certain solvents-gamma-butyrolactone (GBL), *N*,*N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO), respectively. Based on the above characteristics, inverse temperature crystallization (ITC) was first introduced to grow MAPbI₃ single crystals formed at about 190 °C [67]. At the same time, Saidaminov et al. designed inverse temperature crystallization (ITC) for MAPbX₃ perovskites due to their inverse temperature solubility behavior in some solvents [68]. They grew size- and shape-controlled high-quality MAPbI₃ and MAPbBr₃ single crystals within several hours (Figure 2a).

To grow large single crystals and understand their growth mechanism, Liu's group developed the seed-repeated method and harvested the largest MAPbI₃ single crystal, with a size of 71 mm \times 54 mm \times 39 mm, as well as inch-sized MAPbBr₃ and MAPbCl₃ crystals (Figure 2g) [69]. In the process of crystal growth, small perovskite particulates were harvested as seed crystals to keep in precursor solution at 100 °C for 24 h. A seed crystal was placed in precursor solution to keep at 100 °C for 48 h, resulting in the formation of a larger crystal. By repeating the above process, the final large crystals would be produced. Figure 2j shows the absorbance spectra of MAPb X_3 (X = Cl, Br, I) perovskites. A clear band edge without excitonic signature or absorption is shown, indicating high-quality single crystals with low defect concentration. Furthermore, all of the PL spectra of MAPbCl₃, MAPbBr₃, and MAPbI₃ perovskites exhibited narrow PL peaks at \approx 402, \approx 537, and \approx 784 nm, respectively (Figure 2k), and the PL peak values were smaller than the corresponding absorption onsets (431, 574, and 836 nm), indicating their advantageous application in solar cells. The X-ray Diffraction (XRD) measurement displayed that the (200) diffraction peak of MAPbI₃ single crystal showed a FWHM of 0.3718°, which indicated that the single crystal held a respectable crystalline quality. Electric characterization showed that the electron trap was 1.1×10^{11} cm⁻³ for MAPbBr₃ and 4.8×10^{10} cm⁻³ for MAPbI₃. The hole trap densities for MAPbBr₃ and MAPbI₃ were determined to be 2.6×10^{10} cm⁻³ and 1.8×10^9 cm⁻³, respectively. Furthermore, the crystalline MAPbX₃ (X = I, Cl, Br) gave a high carrier mobility of 34 cm²·V⁻¹·s⁻¹, 179 cm²·V⁻¹·s⁻¹ and 4.36 cm²·V⁻¹·s⁻¹. It is expected that such wafer-sized single-crystalline MAPb X_3 (X = I, Cl, Br) with superior properties in terms of defect state and carrier density are promising materials for high-performance optoelectronic devices.

The ITC method is a highly effective approach for growing metal hybrid halide perovskite crystals that possesses a much faster growth rate than that of the typical STL method and has been used extensively to grow single or mixed halide perovskite crystalline materials [67,70–74]. Additionally, the ITC method meets the requirements of FAPbX₃ single crystals. Bakr's group reported the retrograde solubility of FA-based perovskites and grew high-quality crack-free FAPbI₃ and FAPbBr₃ single crystals (Figure 2h,i) [75]. By improving the onset of crystallization temperature, they obtained grain

boundary-free FAPbI₃ crystals within 3 h. Yang's group obtained 5-mm-sized FAPbI₃ single crystals for the first time via a modified ITC method [74]. They first grew the FAPbI₃ seed crystal via a cooling solution method, followed by growing larger single crystals by placing the small seed crystals into the ITC precursor and keeping at 100 °C.



Figure 2. (a) MAPbI₃ and MAPbBr₃ single crystal growth at different time intervals, (b) continuous growth of MAPbBr₃, and (c) crystal shape control of MAPbBr₃ (red) and MAPbI₃ (black). Reprinted with permission from [68], Copyright 2015, Springer; Photographs taken from the as-grown MAPbX₃ crystals: (d,e) MAPbCl₃ (f) MAPbBr₃ (g) MAPbI₃. Reprinted with permission from [69], Copyright 2015, Wiley; (h) FAPbI₃ (black) and (i) FAPbBr₃ (red) single crystal grown by the ITC method. Reprinted with permission from [75], Copyright 2016, Royal Society of Chemistry; UV-vis-NIR absorption spectrum and photoluminescence (PL) properties of CH₃NH₃PbX₃ (X = Cl, Br, I): (j) absorption spectrum and (k) photoluminescence spectrum. Reprinted with permission from [69], Copyright 2015, Wiley.

In addition to the above growth method based upon temperature, the antisolvent vapor-assisted crystallization (AVC) method, a temperature-independent process, was also developed [40]. In AVC, a proper anti-solvent slowly diffuses into the crystal precursor solution, resulting in formation of sizable MAPbX₃. Using the AVC method, Bakr's group [40] gained high-quality MAPbI₃ and MAPbBr₃ single crystals, and implemented a solvent with high solubility for MAX and PbX₂, i.e., *N*,*N*-Dimethylformamide (DMF) or γ -butyrolactone (GBA). Dichloromethane (DCM) acted as the antisolvent to avoid the formation of hydrogen bonds due to its poor solubility for both PbX₂ and MAX, thus minimizing asymmetric interactions with the ions during their assembly into crystal form. This approach created the conditions for the coprecipitation of the ionic building blocks of perovskite. When DCM diffused into DMF or GBA at a slow and controlled rate (Figure 3a), millimeter-sized MAPbBr₃ and MAPbI₃ single crystals were grown. As shown in Figure 3a, to obtain MAPbBr₃ single crystals, PbBr₂/MABr molar ratio of 1:1 was chosen and dissolved in DMF to form the precursor with

 PbI_2 of 0.2 mol·L⁻¹. For MAPbI₃ single crystals, a precursor with PbI_2/MAI molar ratio of 1:3 was dissolved in GBA, and PbI₂ of 0.5 mol·L⁻¹ was prepared. In this case, high-quality MAPbX₃ single crystals were obtained, with super-excellent performance. The absorbance of MAPbX₃ (X = Br^- and I^-) (Figure 3e) exhibited a clear band edge cutoff without excitonic signature that showed a minimal number of in-gap defect states. This confirmed a carrier (holes) concentration of 5×10^9 – 5×10^{10} cm⁻³. The time-dependent PL signals of MAPbI₃ and MAPbBr₃ single crystals were obtained in order to quantify the carrier dynamics (Figure 3f), and showed a superposition of surface components (fast) $\tau \approx 41$ ns and bulk components (slow) $\tau \approx 357$ ns for MAPbBr₃, and fast $\tau \approx 22$ ns and slow $\tau \approx 1032$ ns for MAPbI₃. For MAPbBr₃ single crystals, the carrier lifetime τ was also estimated by transient absorption (TA). It was shown that the fast component amounts to only 3.6% of the total TA signal in MAPbBr₃, and to 7% and 12% of the total PL signal in MAPbI₃ and MAPbBr₃, respectively. As an alternative antisolvent, toluene can also effectively induce formation of MAPbBr₃ single crystals (Figure 3b) with low surface recombination velocity (~(3.4 ± 0.1) × 10^3 cm·s⁻¹) [76] through a process in which the crystal precursor is derived from dissolution of PbBr₂ and MABr (1/1 by molar, 0.1 mol· L^{-1}) in DMF. In another study, diethyl ether was reported as the antisolvent [77], in which HI served as the good solvent instead of organic solvents. Where PbI2 was firstly dissolved in HI solution upon heating to 120 °C, and formed a hot bright yellow solution; to the hot solution was added MAI, which dissolved immediately, leading to the formation of the crystal precursor. X-ray Diffraction (XRD) analysis revealed that an intermediate product of $H_xPbI_{2+x} \cdot xH_2O$ was created because of the coordination between HI and PbI₂. With inflow of diethyl ether into the precursor, $MAPbI_3$ single crystals emerged developmentally. It's worth mentioning that the growth mechanism of halide perovskite single crystals was studied. Recently, Chen et al. reported the growth mechanism of MAPbBr₃ single crystal, which was synthesized by the antisolvent method [78]. The assembly model is shown in Figure 3c. CH₃NH₃Br·PbBr₂·DMF adduct complex was first formed in the precursor solution, and crystallization occurred when the solution was supersaturated. The MAPbBr₃ molecule in the saturated solution condensed into numerous small nuclei with the coalescence of the nuclei into bigger particles. The perovskite particles were gradually self-assembled into a hollow structure. The crystals were twisted, and their faces were peculiarly inclined toward each other. Subsequently, MAPbBr₃ crystals exhibited a layered stacked structure, and continued to grow until the final single crystal was formed. Li and co-workers investigated the crystallization of $MAPbI_{3-x}Br_x$ by adjusting the molar ratio of I/Br in precursor solution [79]. It was found that the crystallization and perovskite morphology were heavily affected by the composition of precursor solutions (Figure 3d). It was reported that Br has a smaller ionic radius and lower solubility in organic solvents because of the stronger bond strength [80]. As a comparison with PbBr₂, PbI₂ has a stronger electron-accepting ability and Lewis acidity [81]. Therefore, it was more likely to form needle crystals of MAPbI_{3-x}Br_x·DMF with high iodine concentration, which might lead to morphology evolution as the molar ratio of I/Br.

Bulk perovskite single crystals can show advanced properties, such as higher carrier mobility, longer carrier lifetime and diffusion length. However, bulk single crystals may cause degradation of device performance, because a thick active layer will increase the charge recombination. In this case, it is desirable to achieve the fabrication of perovskite single-crystal thin films, and thus to enhance the performance of the device. Bakr's group grew MAPbBr₃ monocrystalline film successfully via a cavitation-triggered asymmetrical (CTAC) strategy [82] in which a very short ultrasonic pulse was introduced to a low supersaturation level solution with antisolvent vapor diffusion; perovskite monocrystalline films were able to grow within several hours under the ultrasonic pulse. These obtained films were free of grain boundaries and were homogeneous, with the films having thicknesses ranging from one up to several tens of micrometers, and lateral dimensions varying from hundreds of microns to three millimeters, as shown in Figure 4a.



Figure 3. (a) Chemotic diagram of crystallization process of AVC method. Reprinted with permission from [40], Copyright 2015, AAAS; (b) MAPbBr₃ (red) and MAPbI₃ (black) single crystals grown by AVC. Reprinted with permission from [76], Copyright 2015, American Association for the Advancement of Science; (c) Schematic illustration of MAPbBr₃ single crystal crystallization. Reprinted with permission from [78], Copyright 2018, American Chemical Society; (d) Dependence of ratio of the needle crystals on the bromine concentration of *x*. Reprinted with permission from [79], Copyright 2018, American Chemical Society; (e) Steady-state absorbance and photoluminescence and (f) PL time decay trace on MAPbBr₃ and MAPbI₃ crystal. Reprinted with permission from [40], Copyright 2015, AAAS.

To obtain MAPbI₃ perovskite single-crystalline wafer, Liu's group designed an ultrathin geometry-defined dynamic-flow reaction system (Figure 4c) to obtain single crystals with different thicknesses and shapes (Figure 4d–m) [83]. It was shown that the two glass slides of the reaction system were separated and aligned in parallel by two spacers, leading to the single-crystalline wafer thickness and shape being defined by the spacers and slit channel design. Using the thickness-controllable reaction system, wafer as thin as about 150 μ m with high crystallinity and a low trap state density of 6×10^8 cm⁻³ was prepared.



Figure 4. (a) Optical image and (b) cross-section SEM image of MAPbBr₃ monocrystalline film. Reprinted with permission from [82], Copyright 2016, Wiley; (c) Schematic illustration for the ultrathin single crystal wafer preparation, (**d**–**j**) Photos of the single crystal wafers with different thicknesses and shapes, (**k**–**m**) Cross-sectional view of single crystal perovskite wafers showing different thicknesses. Reprinted with permission from [83], Copyright 2016, Wiley.

Chen et al. reported the controllable fabrication of air-stable, sub-millimeter-size perovskite single-crystalline thin films (SCTFs) [84]. For the preparation process, two flat substrates were clipped together and vertically immersed in perovskite precursor (Figure 5a), the thickness of the solution film could be easily tuned using clipping force, and the resulting SCTF thickness could be adjusted with an aspect ratio of up to 10^5 from nano- to micrometers (Figure 5b). The prepared SCTFs exhibited outstanding air stability and comparable quality to bulk single crystals with trap density (n_{trap}) of 4.8×10^{10} cm⁻³, carrier mobility (μ) of 15.7 cm²·V⁻¹·s⁻¹, and a carrier lifetime (τ_r) of 84 μ s. In addition, perovskite SCTF growth is a substrate-independent strategy, which would offer appealing potentials, such as SCTF/ITO for PSCs, SCTF/PET for flexible devices, SCTF/quartz for optical devices and SCTF/Si for electronic devices, etc.

Recently, Rao et al. developed a space-limited inverse temperature crystallization (SLITC) method, in which the limited spatial module has a tripartite structure: a FTO glass, a U-style thin PTFE, and a PTFE board (Figure 5c). For the preparation of continuous and dense MAPbBr₃ crystal film, the precursor solution was injected into the module and a decreased temperature gradient was applied. As a result, MAPbBr₃ crystal film with a super-large area of 120 cm² and a controllable thickness of $0.1-0.8 \mu m$ was prepared [85] (Figure 5d).



Figure 5. (a) Scheme for growth of perovskite single-crystalline thin films; and (b) Cross-section SEM images and AFM images of MAPbBr₃ single-crystalline thin films with varied thicknesses. Reprinted with permission from [84], Copyright 2016, American Chemical Society; (c) Schematic diagram of the module for growing MAPbBr₃ crystal films; (d) MAPbBr₃ crystal films with a thickness of 0.4 mm and an area about 120 cm². Reprinted with permission from [85], Copyright 2017, Wiley.

Owing to the high photoluminescence quantum yields, metal halide perovskite nanocrystals (Ncs) have also attracted great attention. Using a solvent-induced reprecipitation approach [86], MAPbBr₃ NCs were first synthesized in a process in which octylammonium bromide and octadecylammonium bromide acted as surfactants to stabilize the nanocrystals for up to 3 months. Urban's group reported dilution-induced formation of hybrid perovskite nanoplatelets (NPIs) [87]. This proceeded by fragmentation of the NCs into NPIs, with an excess of organic ligands stabilizing the newly formed surfaces. Such fragmentation was in excellent agreement with the effects of cation intercalation and increased solvent osmotic pressure, resulting in the formation of small nanoplatelets. Vybornyi et al. reported hot injection-based synthesis [88], which was basically an ionic metathesis approach. Varying the amounts of surfactants (octylamine (OAm)/oleic acid (OA) mixture), MAPbI₃ NCs and MAPbBr₃ NPLs, NWs were successfully obtained. It was shown that the resultant NCs had poorer optical properties than those of NCs synthesized by ligand-assisted reprecipitation. Similarly, FA-based nanocrystals have received considerable interest. Protesescu et al. prepared FAPbX₃ (X = Br, I) NCs via a three-step polar solvent-free hot-injection method [89]. NCs with cubic morphology and a high photoluminescence quantum yield (PLQY) of 85% were obtained; however, its potential versatility

was limited by the formation of phase impurities ($NH_4Pb_2Br_5$). Manna's group synthesized FAPbX₃ NCs with excellent phase purity via a modified three-precursor hot-injection technique [71] in which benzoyl halide acted as a halide precursor; thus, the metal cation sources and halide ions were not delivered together, making it possible to work with the ideal stoichiometry of ions.

2.2. Growth of Mixed-Organic-Cation Halide Perovskite Single Crystals

It has been reported that the mixed-organic-cation based on FA and MA halide perovskite integrates nearly all of their advantages, which include extended absorption, decreased trap-assisted recombination and enhanced ambient stability [90,91]. Li et al. fabricated the MA_{0.45}FA_{0.55}PbI₃ single crystal using a modified ITC method [92]. That is, to prepare MAPbI₃/FAPbI₃ (1.0 M) precursor solutions, equimolar PbI₂ and MAI/FAI were dissolved in γ -butyrolactone at 60 °C overnight. Subsequently, the MAPbI₃ and FAPbI₃ solutions were blended in a certain ratio to form the mixed-cation precursor solution. Seed crystals with sizes of 0.5-1 mm were obtained by placing 2 mL mixed-cation perovskite precursor solution in an oil bath at 160 °C for 30 min. To obtain mixed-cation alloy perovskite crystal, a fresh precursor solution containing the corresponding seed crystal was kept at 120 °C for 3 h. Thus, the final MA_{0.45}FA_{0.55}PbI₃ single crystals maintained an impressive stability, and were still able to maintain their original black color after exposure in ambient air for more than 14 months (Figure 6a); however, the α -FAPbI₃ single crystal changed from black to yellow and MAPbI₃ exhibited pale yellow spots on the surface. The carrier lifetime τ of MA_{0.45}FA_{0.55}PbI₃ was characterized by transient photovoltaic (TPV); the TPV curves and corresponding τ are shown in Figure 6d,e. Compared to FAPbI₃ and MAPbI₃, a longer carrier lifetime of 93 µs for MA_{0.45}FA_{0.55}PbI₃ was obtained. In another work, an ITC method assisted by hydroiodic acid for the mixed-organic-cation perovskites $(APbI_3, A = MA^+ \text{ or } FA^+)$ was developed [93]. The given PbI_2 , MAI and FAI were dissolved in GBL with the introduction of appropriate amount of HI, leading to a change in chemical environment in the precursor solution and the formation of APbX₃-GBL, and further to H⁺, MA⁺, FA⁺ and GBL molecules being inserted in the PbI_{2+x}^{x-} layer. Based on the HI-assisted ITC method, FA_(1-x)MA_xPbI₃ single crystals of millimeter size with different compositions were obtained (Figure 6b). By using time-resolved photoluminescence (TRPL) measurements, the carrier lifetimes of fresh $FA_{(1-x)}MA_xPbI_3$ single crystals were investigated. Figure $6f_{,g}$ shows the TRPL spectra of $FA_{(1-x)}MA_xPbI_3$ crystals with different *x* values, and the corresponding lifetimes are summarized in Table 1. It was found that the carrier lifetime of $FA_{(1-x)}MA_xPbI_3$ (x = 0.8–0.95) was significantly improved compared to the counterpart MAPbI₃ single crystal, which disclosed the effective FA⁺ cation doping in MAPbI₃ crystal with respect to carrier behavior.

$FA_{(1-x)}MA_xPbI_3$	x = 0	x = 0.05	x = 0.1	x = 0.15	x = 0.2
$ au_1$ (ns)	91.26	61.43	52.11	27.26	31.58
$ au_1$ (ns)	839.31	689.92	381.86	579.75	236.74
$FA_{(1-x)}MA_xPbI_3$	x = 1	x = 0.95	x = 0.9	x = 0.85	x = 0.8
$ au_1$ (ns)	7	32.45	122	88.05	105.3
$ au_1$ (ns)	145.65	557.5	1074.78	926.39	956.8

Table 1. Lifetimes extracted from the PL spectra of $FA_{(1-x)}MA_xPbI_3$ single crystals with x = 0, 0.05, 0.1, 0.15, 0.2, 0.8, 0.85, 0.9, 0.95, 1.



Figure 6. (a) Photographs of as-prepared MAPbI₃, FAPbI₃ and MA_{0.45}FA_{0.55}PbI₃ single crystals and the same crystals after being stored in air for 14 months. Reprinted with permission from [92], copyright 2017, The Royal Society of Chemistry; (b) $FA_{(1-x)}MA_xPbI_3$ single crystals with different compositions grown via HI-assisted ITC method. Reprinted with permission from [93], Copyright 2016, Royal Society of Chemisty; (c) Schematic illustration of $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ crystal growth process. Reprinted with permission from [94], Copyright 2017 American Chemical Society; (d) Transient photovoltaic curves and (e) the extracted charge lifetime from TPV measurement of MAPbI₃, FAPbI₃ and MA_{0.45}FA_{0.55}PbI₃ single crystals. Reprinted with permission from [92], copyright 2017, The Royal Society of Chemistry; Time-resolved photoluminescence spectra of FA_(1-x)MA_xPbI₃ single crystals (f) with *x* = 0, 0.05, 0.1, 0.15, 0.2 and (g) with *x* = 0.8, 0.85, 0.9, 0.95. Reprinted with permission from [93], Copyright 2016, Society of Chemisty.

Similarly, high-quality mixed-cation and -halide perovskite single crystals, with the formula $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ (x = 0, 0.05, 0.1, 0.15, 0.2), were also successfully grown via the ITC method [94]. The small seeds, grown at 100 °C in the precursor solution, were used to grow crystals, inducing the growth of centimeter sized single crystals, as shown in Figure 6c.

3. Growth of Fully Inorganic Halide Perovskite Single Crystals

Recently, CsPbX₃ perovskites have rightfully been receiving attention because of their promising potential in photovoltaics [95] and bright light emission [96]. Perhaps such fully inorganic halide perovskite can overcome the chemical instability of organic-inorganic hybrid halide perovskite. It was once reported that CsPbX₃ perovskite single crystals could be obtained via the Bridgmann method, a melt crystallization method, which was carried out at a high temperature and with highly pure starting reagents [97–100]. In 2008, for the first time, CsPbCl₃ single crystals were grown with the Bridgmann method using a process in which the precursors of the PbI₂ and CsCl powders were sealed in a quartz crucible under vacuum [98]. In addition, CsPbBr₃ single crystals were also grown using the melt crystallization method [97]. Other than the above, the fast and simple route via solution growth of hybrid halide perovskite single crystals was also used to grow inorganic CsPbX₃ single crystals

using the ITC method. Dirin et al. presented the growth of CsPbBr₃ single crystals under ambient atmosphere using the ITC method [101]. The optimal solvent for the growth of CsPbBr₃ was reported to be DMSO. In particular, a solution of CsBr and PbBr₂ (1/2 by molar), dissolved in a mixed solvent of DMSO with cyclohexanol and DMF, could grow 1–3 nuclei at 90 °C, and further crystal growth could take place without additional nucleation until the temperature increased to 110 °C. As a result, a flat and orange-colored CsPbBr₃ single crystal of ~8 mm in length was obtained (Figure 7).



Figure 7. Photographs of the obtained CsPbBr₃ single crystals. Reprinted with permission from [101], Copyright 2016, American Chemical Society.

The AVC method can be used to prepared inorganic halide perovskite, too. Rakita et al. grew CsPbBr₃ single crystals from a DMSO precursor solution with CsBr and PbBr₂ (1/1 by molar) [102]. The precursor solution was titrated by MeCN or MeOH until a saturated system was achieved. The saturated solution was filtered to use for crystal growth. During the AVC process, MeCN or MeOH was developed as the antisolvent. A balanced antisolvent atmosphere was created, and crystal formation occurred at room temperature; the crystal growth could be accelerated by heating the antisolvent bath. In addition, crystal growth using H₂O as an antisolvent was investigated, and it was found that the orange crystals were inclined to blench. CsPbBr₃ crystal growth via the ITC method was also studied by the same group. To eliminate the formation of undesirable precipitants, they developed a two-step heating cycle. The precursor solution was firstly heated to the desired temperature and allowed return to room temperature under continuous stirring. After being filtered, the final crystalline precursor solution was obtained, and orange CsPbBr₃ crystals were shown after the second heating cycle. It is noted that CsPbBr₃ crystals begin to appear at above 120 °C in the MeCN-saturated solution; however, this can occur at about 40 °C in the MeOH-saturated solution.

Tong et al. reported high-quality colloidal CsPbX₃ (X = I, Br, and Cl) perovskite nanocrystals (NCs) [103]. The synthesis was based on direct tip sonication of precursor mixtures under ambient atmospheric conditions. This method was based on the formation of a metal-ligand complex, which was then further reduced into metal nanoparticles. Urban and Co-workers developed a single-step ligand-mediated synthesis of single-crystalline CsPbBr₃ nanowires (NWs) directly from the precursor powders [104]. Through an oriented-attachment mechanism, the initially formed CsPbBr₃ nanocubes were transformed into NWs, which exhibited strongly polarized emission and could self-assemble at an air/liquid interface.

In addition, $Cs_2AgBiBr_6$, a bismuth-halide double perovskite single crystal was also reported by Karunadasa's group [105]. To obtain the large single crystal, the precursor solution was kept at 110 °C for 2 h, then cooled to room temperature at a cooling rate of 1 °C/h. The results indicated that $Cs_2AgBiBr_6$ crystal had an indirect bandgap of 1.95 eV and a long room-temperature PL lifetime of ca. 660 ns.

The growth methods and properties of as-grown perovskite single crystals are summarized in Table 2.

Single Crystal	Growth Method			Properties		
		Size (mm)	Growth Period	Carrier Mobility ($cm^2 \cdot V^{-1} \cdot s^{-1}$)	Trap State Density (cm ⁻³)	Ref.
MAPbI ₃		2–3	48 h			[60]
CH ₃ NH ₃ PbBr ₃	STL	5	More than 10 days			[60]
MAPbI ₃		10 imes 10 imes 8	-			[61]
MAPbI ₃		12 imes 12 imes 7	2–4 weeks	105 ± 35	10^{10}	[62]
MAPbI ₃		20 imes 18 imes 6	5 days			[63]
CH ₃ NH ₃ PbI ₃ (Cl)		$20\times18\times6$	5 days	167 ± 35	$7.6 imes 10^8$	[66]
MAPbI ₃		$71\times54\times39$		34	$1.4 imes 10^{10}$	[71]
MAPbCl ₃		7	3 days	179	$1.8 imes 10^9$	[71]
MAPbBr ₃	ITC	11 imes 11 imes 4	-	4.36	$2.6 imes10^{10}$	[71]
FPbI ₃		5		4.4	$1.5 imes 10^{11}$	[76]
$MA_{0.45}FA_{0.55}PbI_3$		8	4 h	271 ± 60	$2.6 imes 10^9$	[86]
CH ₃ NH ₃ PbBr ₃	AVC	1.4 imes 1.4 imes 0.7			10 ⁹ -10 ¹⁰	[78]

Table 2. Summary of perovskite single crystal growth methods and properties of as-grown crystals.

4. Application of Halide Perovskite Single Crystals

Through the CATC method, Bakr's group grew hybrid perovskite monocrystalline films and carried out explorative study for the first time on perovskite monocrystalline solar cells with two simple device structures, i.e., ITO/MAPbBr₃/Au and FTO/TiO₂/MAPbBr₃/Au [82]. Figure 8 shows the photoelectric characteristics of those monocrystalline solar cells. Without any HTLs and ETLs, the optimized solar cell of ITO/MAPbBr₃ (4 μ m)/Au offers an ultra-stable photoelectric conversion efficiency (PCE) of over 5% and close to 100% IQE (Figure 8a,c). Furthermore, for the p-n-junction-based architecture, near 100% IQE and higher efficiency (6.5%) than the best HTL-free MAPbBr₃ solar cells was achieved (Figure 8b,d). These significant works made clear that the optoelectronic properties of monocrystalline-film-based devices are superior to their polycrystalline counterparts. Interestingly, based on the bulk single crystal, Huang's group fabricated a lateral-structured device with a maximum PCE of 5.36% at 170 K and a comparable *J*_{SC} to the best thin-film solar cells [106].



Figure 8. Illuminated and dark *J-V* curves, wavelength-dependent *IQE* and *EQE*: (**a**,**c**) ITO-based and (**b**,**d**) FTO/TiO₂-based monocrystalline film solar cells. Reprinted with permission from [82], Copyright 2016, Wiley.

Photodetectors are another device for realizing photoelectric conversion, and have attracted much attention because of their extensive applications, which include biological sensing, camera imaging, missile warning, and communication [107–110]. Organic–inorganic hybrid perovskite single crystals have also been utilized to fabricate photodetectors [111–113]. Lian et al. firstly fabricated high-performance planar-type photodetector on the (100) facet of MAPbI₃ single crystal [61]. The spectral responsivity (*R*) and *EQE*, the crucial parameters for photodetectors, were measured and calculated. For MSCP (MAPbI₃ single crystal photodetector) and MPFP (MAPbI₃ polycrystalline film photodetector), the *R* values were estimated to be 2.55 A W⁻¹ and 0.0197 A W⁻¹, respectively, with the corresponding *EQE* values calculated to be 5.95×10^2 % and 4.59%, respectively (Figure 9a), which are over two orders of magnitude higher than the *R* and *EQE* values obtained for MSCP. Furthermore, the photoresponse times of MSCP (74 µs and 58 µs for the rise time and decay time, respectively) were about three orders of magnitude faster than those for MPFP (52 ms and 36 ms for the rise time and decay time, respectively) (Figure 9b).



Figure 9. (a) Responsivity, external quantum efficiency *EQE*; and (b) Transient photocurrent response for as-fabricated MSCP and MPFP. Reprinted with permission from [61], Copyright 2015, Springer; (c) Time response of the MAPbI₃ perovskite photodetector; and (d) Responsivity of MAPbI₃ single crystal photodetector at different radiance power. Reprinted with permission from [114], copyright 2016, The Royal Society of Chemistry.

Ding et al. fabricated a self-powered MAPbI₃ perovskite single crystal photodetector with Au-Al electrodes [114], which exhibited a fast rise and decay time of 71 μ s and 112 μ s (Figure 9c). A good *R* value of 0.24 A W⁻¹ at the lowest incident power density of 1 × 10⁻⁸ W cm⁻² was demonstrated (Figure 9d).

Liu's group reported a MAPbI₃ single-crystalline wafer photodetector [83] that showed a photocurrent response about 350 times higher than that of the microcrystalline thin film detector. Moreover, nearly 100 photodetectors were fabricated on a piece of single-crystalline perovskite wafer (Figure 10a), highlighting the feasibility of batch-processing integrated circuits on ultrathin single-crystalline wafers. In addition, they fabricated FAPbI₃-wafer-based photodetectors, which exhibited a photoresponse 90 times higher than its thin-film perovskite counterpart. Furthermore, an array of more than 150 photodetectors were also designed on a piece of thin wafer. Using MAPbBr₃ single crystal, Shaikh et al. constructed Schottky-type photodetectors [115]. These devices exhibited response times on the scale of 100 μ s and a photodetectivity of 1.4×10^{10} Jones at zero bias. Recently, narrowband photodetector devices based on large-area MAPbBr3 crystal films have been studied [85], which has enabled high narrow response under a low bias of -1 V, a broad linear response range of 10^{-4} – 10^2 mW cm⁻² and 3 dB cutoff frequency (f_{3dB}) of ~110 kHz. Different from one-component single-crystal perovskite photodetectors, a core-shell heterojunction photodetector based on MAPbBr3 single crystal was developed [116]. It was found that the photodetector offered the feature of self-power and exhibited a peak R of 11.5 mA W^{-1} at zero bias under 450 nm, which was one order of magnitude higher than that of MAPbBr₃ single crystal. The EQE of 3.17% was also much higher than the reported MAPbBr₃ single crystal (0.2%). The high-quality MAPbCl₃ crystals for UV photodetection were grown using DMSO-DMF solution. This demonstrated that the MAPbCl₃ single crystal-based UV-photodetector possessed an on-off ratio as high as 1.1×10^3 and a calculated detectivity of 1.2×10^{10} Jones. Li et al. reported that the mixed cation MA_{0.45}FA_{0.55}PbI₃ perovskite single crystal photodetector [88], which showed high on-off ratio of about 1000, a low detection limit of ~1 nW cm⁻², and a short response time of less than 200 μ s. It is noted that the photodetector showed stable characteristics for a long period at both zero and -1 V bias, as shown in Figure 10d.



Figure 10. (a) Photograph of ≈ 100 photodetectors fabricated on a single-crystalline wafer; (b) *R* and (c) *EQE* of a detector made of single-crystalline perovskite wafer and microcrystalline perovskite thin film. Reprinted with permission from [83], Copyright 2017, Wiley; (d) Stability test of MA_{0.45}FA_{0.55}PbI₃ perovskite single crystal photodetector at 0 V and -1 V bias. Reprinted with permission from [88], copyright 2017, The Royal Society of Chemistry.

Further, owing to the excellent carrier transport properties, metal halide perovskite single crystals can also be used in high-energy ray detectors, which are able to convert some high-energy rays like X-ray and γ -ray photons into charges. Using the MAPbI₃ films, an X-ray detector with responsivity of 1.9×10^{-4} carriers/photon was first reported [117]. Based on bulk MAPbBr₃ single crystal, through structural optimization and surface passivation, Wei et al. fabricated the X-ray detector and obtained a detector with a sensitivity of 80 μ C·mGy_{air}⁻¹·cm⁻² [118].

5. Summary and Future Perspectives

Metal hybrid perovskites have been extensively studied for solar cells, photodetectors, lasing, light-emitting diodes, etc., owing mainly to their excellent semiconductor properties, low cost and facile deposition techniques. It is noted that metal hybrid perovskite single crystals show remarkably low trap-state densities and long carrier diffusion lengths, which can even compare with the best photovoltaic-quality silicon. These properties enable metal hybrid perovskite single crystals to act as desirable semiconductors for optoelectronic applications. This review focuses on the recent progress in the growth and application of different metal hybrid perovskite single crystals. Single- and mixed-organic-cation halide perovskite single crystals can be prepared in solution, with the STL process having been demonstrated to be an effective method. To grow large-sized and high-quality single crystals, the seed-assisted growth method was developed, and centimeter-sized single crystals were obtained. However, STL is a time-consuming process. The ITC and AVC methods are improved processes that have been widely investigated for growth of high-quality single crystals. It is noted that the fully inorganic halide perovskite single crystals can be grown by solution process. The preparation of the above metal hybrid halide perovskite single crystals may contribute to their further application research.

To date, optoelectronic devices based on perovskite single crystals are gradually being considered. The brilliant performance of single-crystal-based photodetectors is further testimony to the benefits of metal hybrid halide perovskite materials. However, the application in solar cells based on single crystals is still limited because of the lack of high-quality monocrystal films with appropriate thickness for perovskite solar cells. In the future, the preparation of high-quality perovskite single crystals with controlled thickness and orientation able to meet the requirements of this application is urgently needed.

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