RESEARCH HIGHLIGHTS

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Single crystals of perovskites

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During last decade, metal halide perovskites (MHPs) have become research hotspot due to their superior optoelectronic properties[1−15]. MHP single crystal was first reported in 1978[16]. Up to now, MHP single crystals with various compositions have been synthesized and characterized. Compared with perovskite polycrystalline films, perovskite single crystals show lower defect density, higher carrier mobility, longer carrier diffusion length. Here, we summarize the growth methods of perovskite single crystals, and discuss their optoelectronic applications, including perovskite solar cells (PSCs), photodetectors (PDs) and light-emitting diodes (LEDs).

A variety of crystallization methods have been developed for preparing high-quality perovskite single crystals[17−21], including inverse temperature crystallization (ITC) method[19], solution temperature-lowering (STL) method[20, 21] and antisolvent vapor-assisted crystallization (AVC) method[22, 23]. ITC method was first proposed by Bakr *et al.* to grow $MAPbX_3$ ($X = Br^-, I^-$) single crystals in 2015[19] (Fig. 1(a)). This method is applied to precursors with inverse solubility in certain organic solvents (i.e., the solubility decreases as temperature increases). Perovskite molecules in complex can be released by raising the temperature, initiating supersaturation and crystallization. For $MAPbI_3$, $MAPbBr_3$ and $MAPbCl_3$, the applicable solvents for ITC method are GBL, DMF and DMSO, respectively. This method is commonly used because it is very simple and quick. For STL method, the supersaturation is achieved by lowering the temperature of a hot saturated solution[20] (Fig. 1(b)). The solvents have increasing solubility with temperature, e.g., HI-based solution. High-quality single crystals can be obtained by precisely controlling the rate of lowering temperature[21]. However, STL method is quite time-consuming. Bakr *et al.* reported AVC method to grow sizable $MAPbX_3$ (X = I or Br) single crystals with volumes exceeding 100 mm^3[22]. The perovskite solution was sealed in an antisolvent-containing container, and the diffusion of antisolvents induces slow and uniform crystallization without changing the temperature (Fig. 1(c)). Ding *et al.* utilized this method to grow lead-free perovskite materials $(NH_4)_3Sb_2I_xBr_{9-x}$ in ethanol solvent[23].

For photovoltaic application, the absence of grain boundary in single crystals lowers the defect density and increases carrier diffusion length, theoretically enabling better device performance. While in practice, it is challenging to obtain single-crystal devices with controllable thickness, negligible surface defects and well-deposited functional layers, which explains their underperformance compared with polycrystalline counterparts. Efforts have been made to thickness control, defect engineering and interface management, pushing the power conversion efficiency (PCE) to over 20%. Bakr *et al.* used space-limited ITC method to grow size-controllable $MAPbI_3$ single crystal[24]. A PTAA-coated substrate was used to cover another PTAA-coated substrate spread with perovskite precursor on the surface, and the complex was then heated slowly. The growth of crystal film was confined by hydrophobic substrates, and micrometers-thick single-crystal film was obtained. With careful separation of two substrates with a blade, good contact between crystal film and transport layer could be ensured, yielding a PCE of 21.09% with a high fill factor of 84.3%. To reduce surface defects caused by MAI escape at high temperature, Bakr *et al.* lowered the crystallization temperature by using mixed solvent, propylene carbonate (PC) and GBL[25] (Fig. 2(a)). The addition of PC can let crystallization to occur at <90 °C. The film exhibited a smooth surface with a uniform thickness of ~20 μm (Fig. 2(b)). The PCE was increased to 21.9%. To further broaden near-infrared (NIR) response, mixed-cation $FA_{0.6}MA_{0.4}PbI_3$ single-crystal films were made[26]. The external quantum efficiency (EQE) spectra showed edge redshifted, increasing short-circuit current density to over 26 mA/cm^2 while maintaining the open-circuit voltage. A PCE of 22.8% was achieved.

Perovskite single crystals have been used in PDs. In 2015, Sun *et al.* first utilized perovskite single crystal to make PDs (Fig. 2(c)), revealing better performance and durability than its polycrystalline counterpart[27]. Under 1 mW/cm^2 light illumination, $MAPbI_3$ single-crystal PD showed 100 times higher responsivity and EQE. To further increase the detectivity and lower the noise, Huang *et al.* made detectors with thin perovskite single crystals, obtaining low dark current, low noise and high detectivity[28]. $MAPbBr_3$ PDs offered a record linear dynamic range of 256 dB, which can be attributed to reduced carrier recombination. In 2016, Huang *et al.* first explored the application of $MAPbBr_3$ single crystal in X-ray detector, achieving a high mobility-lifetime product of 1.2×10^{-2} cm^2/V[29]. Lead-free perovskite single crystals were also used in X-ray detectors. Tang *et al.* used double perovskite

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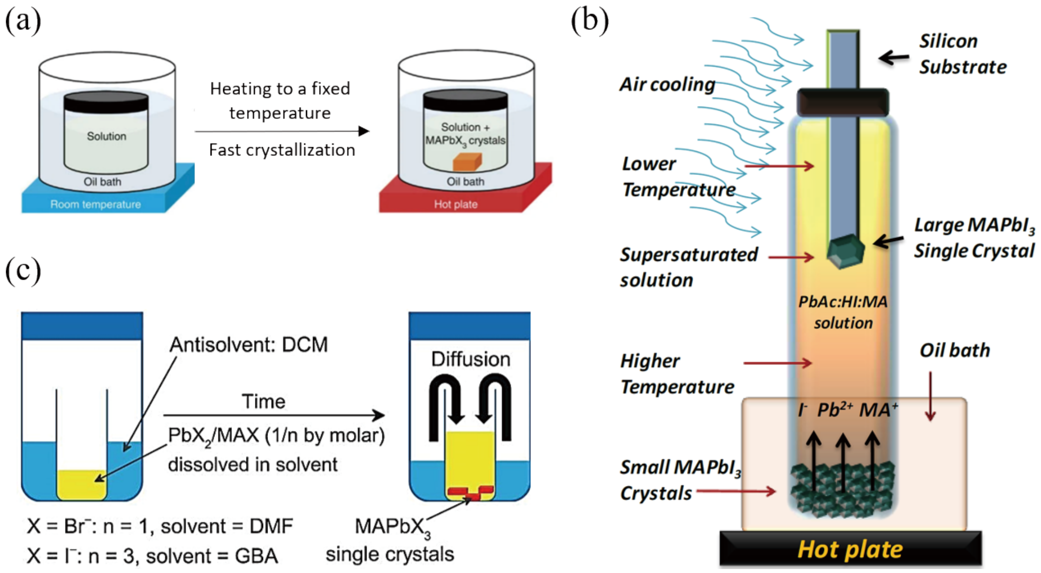

Fig. 1. (Color online) Common solution growth methods for perovskite single crystals. (a) Inverse temperature crystallization method. Reproduced with permission[19], Copyright 2015, Springer Nature. (b) Solution temperature-lowering method. Reproduced with permission[20], Copyright 2015, Science (AAAS). (c) Antisolvent vapor-assisted crystallization. Reproduced with permission[22], Copyright 2015, Science (AAAS).

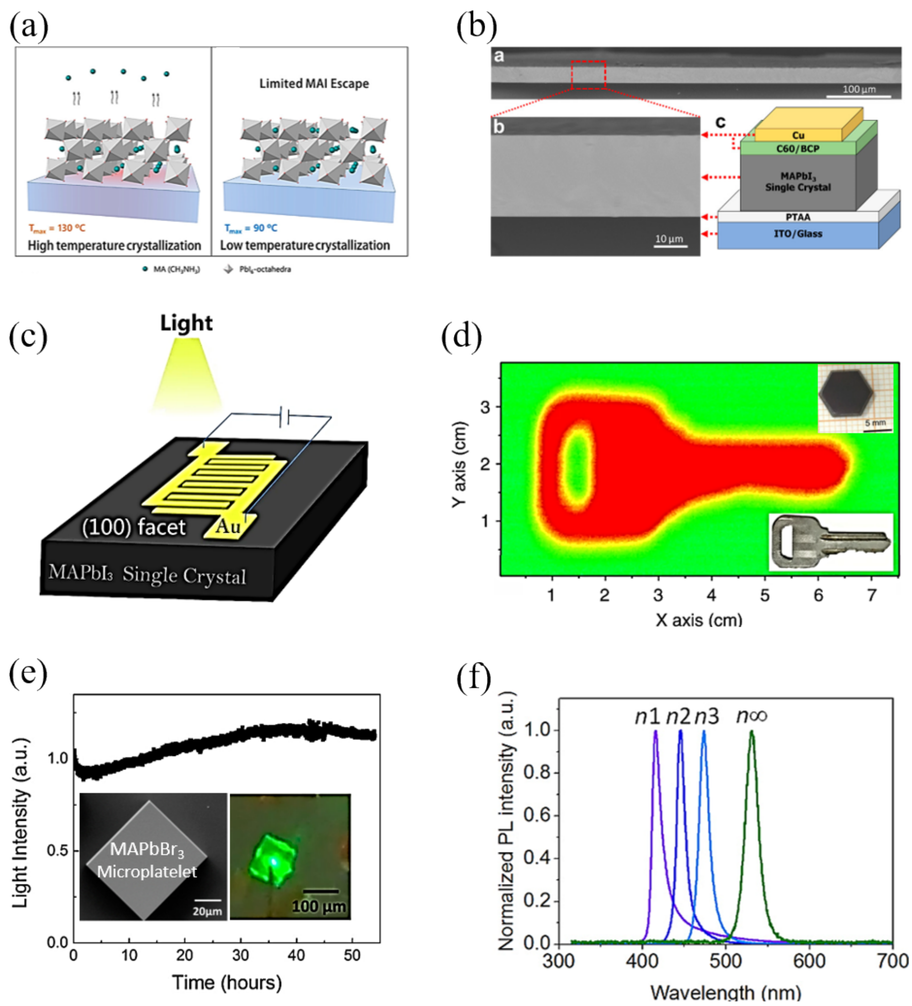

Fig. 2. (Color online) (a) MAI escape from $MAPbI_3$ films in high-temperature and low-temperature crystallization. (b) Cross-sectional SEM images and device structure for $MAPbI_3$ single-crystal PSC. Reproduced with permission[25], Copyright 2020, American Chemical Society. (c) The planar-type photodetector fabricated on (100) facet of a $MAPbI_3$ single crystal. Reproduced with permission[27], Copyright 2015, Springer Nature. (d) The X-ray image for a key by $Cs_3Bi_2I_9$ single-crystal detector (1 × 1 mm^2). Reproduced with permission[32], Copyright 2020, Springer Nature. (e) Emission intensity *vs* time plot for an LED operated at 1 mA current. Inset: SEM image for $MAPbBr_3$ micro-platelet and the image of LED at t = 12 h. Reproduced with permission[33], Copyright 2017, American Chemical Society. (f) Normalized PL spectra for $(BA)_2Cs_{n-1}Pb_nBr_{3n+1}$ single crystals. Reproduced with permission[35], Copyright 2020, Science (AAAS).

$Cs_2AgBiBr_6$ single crystal to make X-ray detectors with a minimum detectable dose rate of 59.7 nGy_{air}/s[30]. Yang *et al.* reported anisotropic X-ray detectors based on $(NH_4)_3Bi_2I_9$ single crystals with a detection limit as low as 55 nGy_{air}/s[31]. Liu *et al.* used refinement solution to get rid of extraneous nuclei and grew large $Cs_3Bi_2I_9$ single crystals[32]. The X-ray detectors showed high sensitivity, low dark current and high thermal stability at 100 °C, being suitable for X-ray imaging (Fig. 2(d)).

Moreover, perovskite single crystal can be a good electroluminescent material. Yu *et al.* first reported LEDs based on $MAPbBr_3$ single-crystal micro-platelets with a simple structure ITO/PVK/Au[33]. The device emitted green light with a luminance of ~5000 cd/m^2, lasting for at least 54 h without degradation (Fig. 2(e)). Then, the electroluminescence blinking behavior of $MAPbBr_3$ single crystal was observed. The device with a structure ITO/$MAPbBr_3$/ITO exhibited a low operation voltage of 2 V and a pure green emission with full width at half maximum of ~20 nm[34]. Nevertheless, the luminescence went through blinking at the crystal edges. The radiative recombination mainly occurred at crystal edges due to spatial confinement effect, but large number of traps and defects also exist at the edges, providing non-radiative paths. The excitons either emitted light or were quenched by the traps at the edges, leading to blinking. Yang *et al.* prepared a series of 2D Ruddlesden-Popper perovskite single crystals with the formula of $(BA)_2Cs_{n-1}Pb_nBr_{3n+1}$[35]. Blue LEDs with high color purity were made *via* a micromechanical exfoliation method. The emission can be tuned across blue light range by varying n (Fig. 2 (f)).

Single crystals of perovskites present application potential in solar cells, photodetectors and LEDs by virtue of superior optoelectronic properties. Various growth methods have been developed to obtain large single crystals with high quality. More efforts will focus on size control, interface modification and long-term stability.

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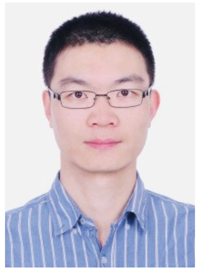

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