Electronic-Grade High-Quality Perovskite Single Crystals by a Steady Self-Supply Solution Growth for High-Performance X-ray Detectors

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High-quality perovskite single crystals with large size are highly desirable for the fundamental research and high energy detection application. Here, a simple and convenient solution method, featuring continuous-mass transport process (CMTP) by a steady self-supply way, is shown to keep the growth of semiconductor single crystals continuously stable at a constant growth rate until an expected crystal size is achieved. A significantly reduced full width at half-maximum (36 arcsec) of the (400) plane from the X-ray rocking curve indicates a low angular dislocation of $6.8 \times 10^{-6}$ cm$^{-2}$ and hence a higher crystalline quality for the CH$_3$NH$_3$PbI$_3$(MAPbI$_3$) single crystals grown by CMTP as compared to the conventional inverse temperature crystallization (ITC) method. Furthermore, the CMTP-based single crystals have lower trap density, reduced by nearly 200% to $4.5 \times 10^9$ cm$^{-3}$, higher mobility increased by 187% to 150.2 cm$^2$ V$^{-1}$ s$^{-1}$, and higher mobility–lifetime product increased by around 450% to $1.6 \times 10^{-3}$ cm$^2$ V$^{-1}$ as compared with the ITC-grown reference sample. The high performance of the CMTP-based MAPbI$_3$ X-ray detector is comparable to that of a traditional high-quality CdZnTe device, indicating the CMTP method as being a cost-efficient strategy for high-quality electronic-grade semiconductor single crystals.

Organic–inorganic hybrid perovskites such as methylammonium lead halide (MAPbX$_3$, MA = CH$_3$NH$_3$+, X = I$^-$, Br$^-$, Cl$^-$) attract wide attention in the field of optoelectronics due to excellent properties. There is also a requirement of high-quality single-crystalline perovskites for fundamental research and in some special applications such as X-ray and gamma-ray detection. The well-grown centimeter single crystals of perovskite prove itself with extremely low trap density of $10^{-8}$–$10^{-10}$ cm$^{-3}$,[17] long diffusion length of 175 µm,[18] high carrier mobility of 164 cm$^2$ V$^{-1}$ s$^{-1}$[18] and long lifetime of 82 µs.[19] For detection applications, halide perovskite crystals may be considered to be the most attractive emerging materials due to the first demonstration of gamma energy resolution capability with the solution-grown method to achieve low cost goal.[15,20] It is surprising that an electronic-grade semiconductor single crystal can be grown by a low-temperature solution-based growth method, which probably owing to a large diffusion velocity of solvated species at growth interface and high formation energies of impurities and intrinsic defects from the viewpoint of kinetic growth mechanism. The history of the synthesis and the crystal growth of organometal halide perovskites crystals could be backtrack to the first report by Weber at 1978.[21,22] However, until 2015, centimeter-scale high-quality perovskite single crystals were grown independently by several groups using

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different approaches. All of the solution-based growth methods developed recently can be grouped into the inverse temperature crystallization (ITC), the anti-solvent vapor assisted crystallization method (AVC), and the cooling temperature methods including bottom seeded solution growth (BSSG) method and the top-seeded solution growth (TSSG) method. These solution methods have grown high-quality and centimeter single crystals of halide perovskite successfully.

However, single-crystal semiconductors such as Si, Ge, GaAs, CdTe, and GaN grown by the traditional melting growth methods often bear superior structure perfection and extremely low defect density. As compared to the general melting methods, the uncontrollable growth, especially the uncontrollable growth rate, may appear to be responsible for the poor structure perfection for single crystals grown by solution-based methods. For example, in the case of ITC or the cooling temperature method, the growth rate decreases with time at the fixed temperature due to the decrease of solute concentration. Therefore, the temperature needs to be adjusted very precisely (less than 5 °C every day) to maintain the growth rate roughly the same. Even worse, for the continuous growth of a crystal with a large size, the as-grown crystal was moved out of the original vial into a larger one with fresh growth solution, severely interrupting the crystal growth and making the growth unstable. Brilliant solutions have already been developed to settle the above problems. Recently, a modified AVC with controlled antisolvent diffusion has been developed to grow a large size of MAPbBr₃ single crystal, making the crystal much more controllable than the conventional AVC method.

In this work, we employed a simple and convenient approach to synthesize high-quality MAPbI₃ single crystals with a size larger than 4 cm. This approach, named after continuous-mass transport process (CMTP), can uninterruptedly provide raw materials for the growth of crystals, and therefore, large single crystals can be grown continuously at a stable growth rate. The crystals grown by CMTP show a much lower angular dislocation density than that of the crystals by ITC, as evidenced by the smaller value and variation (45 ± 9 arcsec) of the full width at half maximum (FWHM) of high-resolution X-ray rocking curve. An improved carrier transport of the CMTP MAPbI₃ single crystal was also confirmed by admittance spectroscopy, attributing to a low defect density. The performance of MAPbI₃ X-ray detector grown by the CMTP method can be comparable to that of an energy-resolved high-quality CdZnTe device, also indicating excellent optoelectronic properties of the CMTP perovskite single crystal.

Before the growth of the large crystal, the seed crystal should be prepared by using the ITC method firstly. In this stage, a large number of small (∼1–2 mm in size) seed crystals were harvested by heating the MAPbI₃ precursor solution to 100 °C. Then, only one seed crystallite was transferred to a fresh MAPbI₃ precursor solution in Cylinder A of an H-like apparatus as shown in Figure 1a and Figure S1 (Supporting Information). For comparison, the improved ITC method with temperature gradient crystallization was used to prepare the reference ITC large crystal sample, by which only Cylinder A is used and the growth begins at 84 °C then slowly increase to 96 °C in 2 °C day⁻¹ during the following six days.

The whole growth model of the solution-based method can be demonstrated using the dissolution–nucleation diagram as shown in Figure 1b. The experimental solubility curve (Figure S2, Supporting Information) and the schematic super-solubility curve divide the diagram into three regions, i.e., the unsaturated, supersaturated, and metastable regions. It is supposed that the spontaneous nucleation occurs only inside the supersaturated region. In our experiment mentioned above, the seed growth at 100 °C occurs in the supersaturated region, as denoted by the grey dot and characterized with the appearance of large numbers of small crystals. For the growth of one large single crystal in a space-limited vessel, the supersaturated

Figure 1. Crystal growth process. a) Schematic illustration of the continuous-mass transport process. b) Dissolution–nucleation diagram. Purple curve: Solubility of MAPbI₃ in GBL. Blue dash curve: Super-solubility curve. Red short dot line: CMTP. Black arrow with dot line: ITC at the same growth temperature of 84 °C. Light blue arrow with dot line: ITC with temperature gradient crystallization from 84 to 96 °C. c) Crystal growth rate by different methods. Inset: Photographs of the as-grown crystals by CMTP.
region should be avoided to reduce the continuous emerging of a large number of small crystals, and the metastable region is much more suitable for the growth of large crystal.

The growth procedure of the reference ITC sample can then be explained in Figure 1b. If the ITC growth is maintained at the constant temperature in the metastable region, the concentration of the solution in a space-limited vessel would decrease with the crystal growth due to the consumption of solute, as indicated by the black arrow with dots line in Figure 1b. The growth rate (Figure 1c) hence decreases accordingly. Thus, the solution temperature should be gradually increased in order to keep the growth of crystal continuous, as indicated by the light blue arrow with dots line in Figure 1b. However, the corresponding growth rate (Figure 1c) is still disrupted because the growth rate is not simply linearly increasing with temperature even in an ideal case. The uncontrollable growth rate by the ITC method therefore fails to keep the whole growth process always at the same growth rate.

Could we keep the growth rate stable as a true constant continuously? Actually, since the crystal growth is a spatially discontinuous and heterogeneous process, the growth rate of solution crystals is determined by the interface dynamics theory suggested by Brice.

\[
f = \frac{V_m D}{\delta} (C_\infty - C_s)
\]

(1)

where \(f\) is the crystal mass growth rate, \(\delta\) is the solute boundary layer thickness, \(D\) is the diffusion coefficient which mainly determined by growth temperature, the adopted solvent and solute, \(V_m\) is the molar volume, \(C_\infty\) is the solute concentration of the solution, \(C_s\) is the equilibrium concentration of the solute (solubility curve).

As indicated by Equation (1), if we can keep a stable growth interface between crystal and solution, especially for the concentration distribution around as-grown crystal that always remains, then the growth rate \(f\) would be kept as a constant and the growth of crystal would be stable continuously. So, how can we maintain the concentration during crystal growth? The key point is that the solute should be supplied from somewhere else continuously.

Therefore, we added another Cylinder B connected with Cylinder A by horizontal feed through as a solute supply region to store and transport raw material (nutrient), as shown in Figure 1a. The solvent in Cylinder B dissolves the nutrient until it reaches saturation. Then, the solvated species can then be transported from Cylinder B to Cylinder A through natural fluid convection driven by a concentration gradient. Then the solvated species in Cylinder A become metastable, come out of solution, and crystalize on the seed. The fluid convection repeats as long as the nutrient is present in Cylinder B.

Suitable growth temperature and the temperature difference between Cylinder A and B should be chosen to yield an expected growth rate. Here, in our experimental approach, we found an optimized growth temperature of Cylinder A to be 84 °C, which is 20 °C higher than that of Cylinder B (64 °C). The growth rate shown in Figure 1c can then be stable at around 4 mm day\(^{-1}\), measured by the maximum of longitude length of as-grown crystal every day. Actually, the temperature difference between two cylinders should be kept below 30 °C to avoid Cylinder A into the supersaturation region, which results in plenty of small crystals in Cylinder A.

The key feature of this process is that the consumption of solvated species can be supplied by itself through the continuous mass transport process (CMTP) from Cylinder B. The growth rate can then be kept as a constant during the whole process, and therefore the stable growth can be achieved continuously until the expected size of crystal is obtained. Moreover, this CMTP process may be more suitable for the growth of alloy and doped single crystal since it can maintain all kinds of solutes concentrations in solution by sufficient nutrient supply even for a large segregation coefficient of alloy and doped elements.

In addition, our CMTP method can be applied not only in the ITC method, but also the cooling temperature method in principle. The ITC method was adopted here because it is a much more convenient and simple approach than other methods, such as the cooling temperature method and AVC method. For instance, the severe corrosion to the growth equipment from the haloid acid often occurred during the cooling temperature process, and hence may lead to the additional impurity into the as-grown crystal.

A typical large crystal with a size of around 4 cm × 3.5 cm × 1.2 cm, grown by the CMTP method, is shown in the inset of Figure 1c. From optical microscopy and naked-eye observation, it seems no obvious difference between the CMTP sample and the ITC sample. Most of the large crystals grown by both methods exhibit rhombic hexagonal octahedron geometry, and the surface of the freshly grown crystals appears to be black and shiny.

For the study of structure imperfection, X-ray diffraction measurements are powerful methods. Firstly, the phase purity of all the as-grown crystals can be confirmed by powder X-ray diffraction, for which the MAPbI\(_3\) powder is milled from large crystals. The main peaks for the as-prepared CH\(_3\)NH\(_3\)PbI\(_3\) powder are at \(2\theta = 14.11^\circ\), 20.04\(^\circ\), 28.41\(^\circ\), and 40.41\(^\circ\), corresponding to the (110), (200), (220) and (400) plane of the tetragonal perovskite structure (Figure S3, Supporting Information). The \(0-2\theta\) X-ray measurement for the surface growth plane of the crystal shows only two sharp diffraction peaks from the (200) and (400) planes, indicating the achievement of single crystals (Figure S3, Supporting Information). Note also that both the ITC and CMTP samples show no clear difference by the power and growth plane XRD scans. Then, the (400) peaks were further examined carefully using double-axis high-resolution X-ray rocking curve (Figure 2a,b). The best FWHM of the peak is measured to be 36 arcsec for the crystal grown by CMTP, far better than 152 arcsec for our best reference ITC sample and those for the crystals grown by ITC methods.[17,32,33] Note that the effect of growth temperature on the quality of MAPbI\(_3\) single crystal was not significant. As shown in Figure S4 (Supporting Information), the FWHM of...
the XRC for the ITC sample grown in the temperature range (74–86 °C) is around 136 arcsec, slightly smaller than the best value of sample grown in the temperature range (84–96 °C), but still nearly four times larger than that of the best CMTP samples grown at 84 °C. So, the quality of crystal was improved by not the growth temperature but the stable growth rate.

An improved FWHM for MAPbI3 single crystal has also been reported by Yan’s group using a different approach by the cooling temperature method (based on the HI acid solution) rather than the ITC method,[34] and most reported results for the ITC MAPbI3 single crystal were all around 180–250 arcsec,[32,33,34] as listed in Table S1. Even worse, the FWHM for the large ITC MAPbI3 single crystal was reported to be about 0.3718° (1338 arcsec), likely due to the unstable growth when the crystal was repeatedly moving out of the original vial into a larger one, severely interrupting the crystal growth.[30] This large FWHM further confirms the importance of stable growth.

The FWHM broadening of the measured rocking curve, which can be defined as $\beta$, is determined by several factors including the intrinsic width for the diffractometer, the angular rotation at dislocation, strain surrounding dislocation, epitaxial film thickness, and the curvature of crystal specimen. The intrinsic broadening determined by diffractometer and the diffraction plane of the measured crystal is generally below 5 arcsec and can often be neglected. The last three factors including strain, film thickness, and curvature are mostly resulted from the epitaxial film, and will not be discussed in a thick single-crystal case. Therefore, the broadening of the rocking curve is mainly caused by the angular rotation at dislocation. This broadening due to angular rotation is associated with subsidiary mosaics which are tilted with respect to each other, as shown in Figure 2c. The measure FWHM is related to the mean disorientation between mosaics which can be determined by the density of dislocations arranged in random network. Hence, the dislocation density can then be estimated by the following equation[35]

$$D = \beta^2 / (4.36b^2)$$

(2)

where $D$ is the dislocation density and $b$ is the length of the Burgers vector, assuming that the orientations of the mosaics have a Gaussian distribution. A calculated low dislocation density of 6.8 × 10^8 cm^-2 for the CMTP sample is obtained, much lower than 2.2 × 10^8 cm^-2 for the ITC sample. Unfortunately, these dislocation densities cannot be confirmed through direct SEM or optical microscopy observation using a defect-sensitive etching process, since a suitable etching solution for MAPbI3 is still lacking up to now.

These results demonstrate that the stable growth rate can result in the improvement of structure perfection while the unstable growth may lead to much more structural inconsistency like angular dislocations between tilted mosaics. The varied growth rate may result in a different diffusion behavior of species on growth surface, leading to more tilted mosaics, as shown in Figure 2c. This FWHM value of 45 ± 9 arcsec and the angular dislocation of 6.8 × 10^8 cm^-2, are comparable to those commercial electronic-grade inorganic semiconductor like GaN (112–204 arcsec), CdTe (7–65 arcsec), and InP (12–32 arcsec), and Ga2O3 (46 arcsec) single crystals grown by melting method.[16–39] indicating the achievement of high-quality single crystals by solution method. Moreover, the large FWHM variation of the ITC samples also implies that the unstable growth rate in the ITC process strongly influence the nucleation and growth.

All the ITC and CMTP samples show similar optical properties including absorption, transmission, and diffuse reflection. As shown in Figure S5a (Supporting Information), the crystals exhibit strong absorption across the entire visible spectrum, and a sharp absorbance band edge cutoff of 854 nm can be observed without excitonic signature or transmittance tail.[26] The as-grown MAPbI3 single crystal gives a bandgap of 1.45 eV by the direct-gap Tauc plot, as shown in the inset of Figure S5a (Supporting Information). This result is in a good agreement with the reported values of single crystals grown by other solution methods like ITC,[40] and significantly smaller than the value measured using the MAPbI3 thin films.

The steady-state photoluminescence (PL) spectrum of the grown MAPbI3 single crystals excited using a 405 nm laser is shown in Figure S5b (Supporting Information). The broad emission spectrum (from 700 to 850 nm) suggests that near-edge defects levels related to surface states or vacancies take part in the emission process.[41] The emission peak is located at 784 nm for CMTP and 792 nm for ITC, both smaller than the absorption onsets, indicating that the lights of PL due to the excitation can be extinguished by themselves.[42] Note that the blueshifted PL peak may also indicate a lower trap density in these crystals grown by CMTP than that by ITC.[38,39,42,43]

As compared to optical properties, the electrical properties of single-crystal semiconductor are supposed to be much more...
sensitive to the quality of the single crystals and could be the indication of crystal perfection. Especially, the energy resolution of alpha particles and gamma-ray spectra is even more sensitive to defects.\cite{13,15} The diagram of the measurement setup is shown in Figure S6 (Supporting Information), with gamma and alpha radiation from a 1 $\mu$Ci $^{241}$Am source. The obtained results demonstrate that MAPbI$_3$ single crystals are capable of detecting energy-resolved high energy particles.\cite{44–46} The best alpha particle resolution of detector grown by CMTP is around 16.1% at room temperature in vacuum, much higher than the resolution of around 29.6% for detector grown by ITC (Figure 3a). A typical gamma-ray energy spectrum (Figure 3b) was acquired by the CMTP detector at a low temperature of 253 K and at a high voltage of 200 V, while no distinct peak was observed in the energy spectrum acquired by MAPbI$_3$ detector grown by ITC. The above results strongly reflect the fact of a much reduced defect density and enhanced carrier transport properties in the CMTP sample due to the improved structure perfection by the continuously stable growth method.\cite{9}

We employed a time of flight (ToF) method to measure carrier transport parameters including mobility and mobility–lifetime product based on the impact of alpha particles from the radiation of $^{241}$Am source.\cite{38,47} In an ideal case, voltage sensitive charge collecting circuit will have a voltage signal that firstly rises linearly with time and then keeps at a maximum signal. The inflection point represents the transit time of the drift of electrons across the sample. It is worthwhile noting that the hole mobility and $\mu \tau$ product value evaluated below are much closer to the true value at a high bias voltage in the MAPbI$_3$ case because the electric field is much more uniform under a deep fully depletion state of device, while electron mobility and $\mu \tau$ product value are difficult to be precisely measured due to

Figure 3. The carrier transport properties. a) Alpha photon-radiation spectra emitted from $^{241}$Am at room temperature. b) Typical gamma-radiation spectrum recorded with MAPbI$_3$ SCs at a low temperature of 253 K. c) The ToF transient curves of detectors. d) Hole drift velocity as a function of electrical field strength. e) The hole mobility–lifetime products of MAPbI$_3$ detectors fitted by using the single-carrier Hecht equation. f) The trap density of states (tDOS) measured by admittance spectroscopy measurement.
p-type metal–semiconductor Schottky diode at interface, which will be discussed later by X-ray photocurrent of MAPbI$_3$.

A typical ToF transient curve in oscilloscope is shown in Figure 3c. Experimentally, the transit time $T_{tr}$ is defined as the time taken from 10% to 90% of the amplitude rise time. Then, assuming the materials with a uniform electric field distribution inside, the mobility can be fitted by the following formula

$$d/T_{tr} = \mu E$$

(3)

where $d$ is the thickness of device, $\mu$ is hole mobility in this case, $E$ is the mean electric field across the device. The top box chart in Figure 3d depicts that the mobility of as-grown crystal by CMTP is about 150.2 cm$^2$ V$^{-1}$ s$^{-1}$, larger than 80.5 cm$^2$ V$^{-1}$ s$^{-1}$ of that by ITC. The $\mu \tau$ product values shown in Figure 3e are estimated in terms of the maximum signal amplitude with applied voltage using the Hecht equation. The device grown by CMTP exhibits $\mu \tau$ product of 1.6 $\times$ 10$^{-3}$ cm$^2$ V$^{-1}$, which is about five times higher than that by ITC.

Note that the values of mobility and $\mu \tau$ product can be varied strongly with different measurement methods adopted, as listed by Table S1 (Supporting Information), and a similar measurement result should be better adopted for comparison. The mobility of MAPbI$_3$ for a ITC sample by a ToF was reported to be 48 cm$^2$ V$^{-1}$ s$^{-1}$, almost half-lower than 80.5 cm$^2$ V$^{-1}$ s$^{-1}$ of our sample by ITC. A large variation of the $\mu \tau$ product in the range of 2–180 $\times$ 10$^{-4}$ cm$^2$ V$^{-1}$ were reported by photocurrent measurement. However, the $\mu \tau$ product of 3.4 $\times$ 10$^{-4}$ cm$^2$ V$^{-1}$ for our ITC sample by alpha particle impact transient spectra is in agreement with the value of 8 $\times$ 10$^{-4}$ cm$^2$ V$^{-1}$ for the ITC MAPbI$_3$ sample measured from $^{241}$Am $\gamma$ ray spectra.

This high $\mu \tau$ product for the CMTP MAPbI$_3$ single crystal is comparable to or even better than the mostly-reported values of the commercial nuclear detector materials such as CdZnTe, HgI$_2$, and TIBr indicating an electronic-grade semiconductor material achieved.

Fundamentally, the $\mu \tau$ product is determined by the level and density of defects, which is seriously responsible for carrier transport process. These defects also cause the incomplete collection of charge signals in detector and affect the energy resolution of the radiation detector sensitively. The admittance spectroscopy measurement provides the trap level and trap density of states (tDOS) in the single-crystal devices, derived from the frequency dependent capacitance. The spectra of tDOS in the range of 0.05–0.20 eV (Figure 3f) exhibit the highest peak at around 0.159 eV. There are still no other reports about experimental defect levels in the MAPbI$_3$ perovskite single crystal, while a similar defect state of 0.167 eV above valence band is also found in the MAPbI$_3$ films by Duan et al., probably ascribed to iodine interstitials according to density functional calculations. The integrated tDOS of about 4.5 $\times$ 10$^{10}$ cm$^{-3}$ eV$^{-1}$ inside the whole range of bandgap can be roughly deduced from the average value of 0.05–0.20 eV, which is far smaller than that of MAPbI$_3$ thin film with $\sim$10$^{16}$ cm$^{-3}$ eV$^{-1}$ but similar with other reports about MAPbI$_3$ single crystal using trap filling limit voltage ($\sim$0.6 $\times$ 10$^{-3}$–36 $\times$ 10$^{-9}$ cm$^{-3}$ eV$^{-3}$). A smaller trap density for the CMTP sample, confirmed by the results of drive-level capacitance profiling (Figure S7, Supporting Information) implies a better carrier transport and a longer lifetime, as evidenced above by the mobility and $\mu \tau$ product measurement, and well in consistence with the structure imperfection information from the X-ray rocking curve results. Note also that the trap density may come mostly from point defects like I interstitials, and are not directly related to angular dislocations.

Excellent carrier transport properties of the CMTP MAPbI$_3$ single crystal may exhibit high performance in optoelectronic devices. Moreover, a high X-ray absorption coefficient, resulting from the heavier atomic number Z of I and Pb, suggests a promising X-ray detection material for MAPbI$_3$ single crystal. Then, a X-ray detector based on the Au/MAPbI$_3$/Au structure is demonstrated in Figure 4. It is better to compare X-ray detector characteristics directly with high performance material, and therefore we choose a 1 mm-thick high-quality Cd$_{0.9}$Zn$_{0.1}$Te single crystal grown by a vertical Bridgeman melting method as a reference sample to evaluate the performance of MAPbI$_3$ detector. Two 50 nm Au electrodes with 2 $\times$ 2 mm$^2$ were used to deposit on the surface of MAPbI$_3$ and CdZnTe single crystal. This high-quality CdZnTe device exhibits a high energy resolution of around 5% measured by a $^{241}$Am 59.5 eV gamma-ray source in Figure S8a (Supporting Information), indicating a high capability of transporting the photo-generated carriers and thus an excellent mobility–lifetime product value (Figure S8b, Supporting Information).

The nonlinear behaviors for all the dark current curves in Figure 4a indicate back-to-back Schottky contacts for all samples. A high applied voltage is often adopted to measure the leakage since the X-ray and gamma-ray detectors achieve high performance generally at a high voltage, but the leakage at high voltage was seldom reported in the perovskite single-crystal case. The CdZnTe single crystal shows the lowest leakage current of around 78 $\times$ 10$^{-9}$ A cm$^{-2}$ at 200 V, about one order of magnitude lower than that of the CMTP-based MAPbI$_3$ sample. Note that the leakage current of 6.2 $\times$ 10$^{-8}$ A cm$^{-2}$ at 200 V for the CMTP-based MAPbI$_3$ device here is likely the best value of MAPbI$_3$ materials reported up to now, as listed by Table S1 (Supporting Information).

The carrier transport of the MAPbI$_3$ devices can be illustrated by the energy band diagram in Figure S9 (Supporting Information). At both positive and negative bias, only one Schottky is on while the other is off, leading to a limited leakage current by the interface depletion region. The dark current of the CMTP sample increases with bias voltage much more slowly than that of the ITC sample. This result may imply that there are less soft impact ionization centers in the CMTP sample, likely responsible for the higher resistance at high voltage and a better energy resolution for the nuclear detector.

With an applied positive bias, the photocurrents for both the CMTP and ITC sample in Figure S10 (Supporting Information) are much larger than that with a negative bias. This can be explained by the energy band diagram in Figure S9 (Supporting Information). With a positive bias, the depletion region located on the illumination side becomes wider while the other depletion region becomes narrower, so the electron-hole pairs generated only on the illumination side have a large chance to be separated by a strong electric field and move to the opposite sides. In contrast, with a negative bias, the electron-hole pairs generated only at the illumination side are far away from the depletion region. This high-quality CdZnTe device exhibits a high energy resolution.
layer and experience a weak electric field, and thus tend to be recombined. So, we can observe a non-symmetry photocurrent with a larger photocurrent at a positive bias (Figures S10 and S11, Supporting Information). This phenomenon also reflects a p-type semiconductor for this metal-semiconductor heterojunction, leading to a hole-determined photocurrent. In contrast, the CdZnTe device exhibits a large photocurrent at a negative voltage, showing an electron-determined photocurrent [55] (Figure S11, Supporting Information).

Under soft X-ray irradiation with a Cu Kα peak energy at 8 kV, a photocurrent of about $3.8 \times 10^{-5}$ A cm$^{-2}$ at an electric field of 100 V cm$^{-1}$ for the CMTP MAPbI$_3$ device can be seen in Figure 4b, slightly higher than $1.8 \times 10^{-5}$ A cm$^{-2}$ for the CdZnTe device and around one order of magnitude higher than $2.2 \times 10^{-6}$ A cm$^{-2}$ for the ITC device in this work. A higher photocurrent of the CMTP MAPbI$_3$ device can also be seen clearly with different X-ray exposures (Figure 4c) and switch curves with time (Figure 4d). The mobility–lifetime product can be estimated from the fitting of photocurrent curve in Figure 4b by the Hecht equation mentioned above, but this value is varied a lot with intense irradiation because largely injected photo-generated carriers at the surface may not only interfere electric field distribution but also lead to an illumination-determined lifetime. Nevertheless, a distinct knee point at a lower voltage can still indicate a higher mobility–lifetime product for the CMTP devices than those for the CdZnTe and ITC devices.

After we evaluated the X-ray performance by directly comparing the MAPbI$_3$ with a high-quality CdZnTe, we can see that the CMTP device shows an even better charge collection efficiency than that of a high-quality CdZnTe device, reflecting excellent photo-generated carrier transport properties of CMTP MAPbI$_3$ single crystal. This excellent carrier transport probably results from a reduced defect density, confirmed directly by a low trap density and dislocation density of the CMTP-based MAPbI$_3$ single crystal due to continuously stable growth. However, as compared to the CdZnTe device, a high leakage current of MAPbI$_3$ device may lead to a poor gamma-ray detection, and many works still need to be done to further reduce the leakage current and improve the lowest detectable dose.

In summary, a simple and convenient approach has been designed to achieve high-quality MAPbI$_3$ single crystals with large size. This approach can uninterruptedly provide raw materials for the growth of crystals by a continuous-mass transport process, and therefore, large single crystals can be grown continuously at a stable growth rate. Compared with the crystal grown by ITC method, the crystal grown by CMTP shows a much lower dislocation density ($6.8 \times 10^{6}$ cm$^{-2}$, nearly two orders of magnitude lower), a higher mobility (150.2 cm$^2$ V$^{-1}$ s$^{-1}$, nearly 187%), a higher mobility–lifetime product ($1.6 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, about 450%), and a lower defect density ($4.5 \times 10^9$ cm$^{-3}$, nearly one order of magnitude lower). The high performance of MAPbI$_3$ X-ray detector grown by the CMTP method can be comparable to that of high-quality CdZnTe device. Moreover, this CMTP method is also a low temperature, low cost approach which is suitable for mass production of high-quality single crystals targeting at photoelectronic sensing applications.
Experimental Section

Synthesis of CH$_3$NH$_3$I Powder: The CH$_3$NH$_3$I powder was synthesized as reported previously by reacting methylamine (33 wt% in ethanol, Sigma-Aldrich), with hydroiodic acids (45 wt% in water, with 1.5% hypophosphorous acid, Sinopharm) in a 100 mL round-bottom Cylinder at 0 °C for 2 h with stirring. After reaction, the white precipitate of CH$_3$NH$_3$I were collected using a rotary evaporator through carefully removing the solvents at 50 °C. The white precipitate was re-dissolved in absolute ethanol and precipitated with the addition of diethyl ether, and this procedure was repeated twice. The final CH$_3$NH$_3$I powder was collected and dried at 60 °C in a vacuum oven for 24 h.

Perovskite Precursor Solution Preparation: To form the non-stoichiometric CH$_3$NH$_3$PbI$_3$ precursor solution, as-prepared methylammonium iodide and lead (II) iodide (99%, Sinopharm) were dissolved in anhydrous γ-butyrolactone (GBL) (TCI) at a 1:3 molar ratio of MAI to PbI$_2$. The final concentrations were 1.54 M lead iodide and 1.99 M methylammonium iodide, respectively. The mixture solution was stirred at 60 °C overnight in the N$_2$-filled glovebox to reduce the oxidation of I$_2$ to I$_3$.

Seed Crystal Preparation: A large number of small (∼1–2 mm in size) seed crystals were grown by inverse temperature crystallization (ITC). The as-prepared perovskite precursor solution was stayed at 75 °C, then slowly increased 5 °C every 20 min, and till to 90 °C the seed began to appear. Then the temperature was increased to 100 °C, and the seed crystals could grow for 20 min.

Large Crystal Growth: For the continuous-mass transport process, the seed was transferred to Cylinder A of a customized and grind arenaceous sealed H-like apparatus filled with perovskite precursor solution, while transferring the extra-complexed crystals to the raw material supply bottle of the H-like device. The seed was transferred in the glovebox to avoid exposure to air directly, and then the system was put into the oil baths in air to grow the single crystal. The growth Cylinder A was heated to 84 °C and maintained at this temperature, and the raw material supply Cylinder B was maintained at 64 °C, so that the solution in the crystal growth bottle had been in a supersaturated state. During the growth of single crystal, the raw materials in Cylinder A continue to be consumed, and simultaneously the raw materials will be continuously supplied from Cylinder B by a nature fluid convection due to concentration difference. With self-supply of raw materials from Cylinder B to Cylinder A, the crystals can be sustained at a stable growth rate.

For the improved inverse temperature crystallization with temperature gradient, the seed was transferred to the growth cylinder A of an H-type apparatus filled with perovskite precursor solution, while Cylinder B was not used. The growth cylinder A was heated to 84 °C firstly, then slowly increased to 96 °C in 2 °C day$^{-1}$ during the following six days.

Solubility Test: The mixtures of MAI and MAPbI$_3$ powder with mole ratio of 0.3:1 was used for the solubility test, while MAPbI$_3$ powder was obtained through grinding as-grown crystals. MAI and MAPbI$_3$ powders were set in a vial placed into an oil bath. The system was heated to specific temperature, such as 40 °C, and small amount of GBL was started to be added, 50 µL by 50 µL, while stirring. When the solute was completely dissolved within two hours after the amount of solvent was dropped into the solution, it was considered to be exactly saturated. The same process was repeated at different temperatures. The introduction of 30 mol% excesses of MAI powder has changed the dissolving characteristic and increased the solubility of MAPbI$_3$. The same solubility test was performed both for the mixture with 10 mol% excesses of MAI and MAPbI$_3$, without excess of MAI.

The upper boundary of the metastable region was roughly estimated by using the spontaneous crystallization temperature of solutions at different concentrations. This upper boundary was treated as a schematic super-solubility curve.

Characterization: Powder XRD patterns were collected using Rigaku D-max III X-ray diffractometer equipped with a Cu tube operated at 40 kV and 30 mA. High-resolution X-ray diffraction measurement was taken using X’Pert MRD, with Cu Kα line operated at with V = 40 kV and I = 20 mA. The UV-Vis transmittance spectra were measured at room temperature using a Perkin-Elmer Lambda 950 UV–vis–NIR spectrophotometer with scan speed 300 nm min$^{-1}$ and slit width quantitative 5 nm in the wavelength range 500–900 nm at room temperature. UV–vis absorbance spectrum was measured in the reflection mode with an integrating sphere attachment operating in the 500–1100 nm region, analyzed through the Kubelka–Munk equation. A highly refined barium sulfate (BaSO$_4$) plate was used as the reference (100% reflectance). The steady-state photoluminescence (PL) was measured at room temperature using the 405 nm laser beam.

The photocurrent–voltage (I–V) curves were measured (2400 Series Source Meter, Keithley Instruments Inc.) by using a 671 nm laser beam. The time dependent photoresponse signal was recorded by a 1 GHz digital oscilloscope and a Keithley 428 current amplifier. A Cu K$_\alpha$, 8 keV X-ray source, which was generated by a Rigaku X-ray diffractometer, was used to characterize detector. The dose rates were modulated by adjusting the X-ray tube current. X-ray dose rates were corrected through a calibrated CdZnTe detector. The X-ray generated photocurrent was measured by a Keithley 2400. All the optoelectronic properties were measured under the atmosphere environment. Typical thickness of single crystals used for I–V measurement and solid-state α particle and gamma-ray energy spectrum measurements were 1–2 mm. These crystals were sandwiched between the rectangular electrodes (2 mm × 2 mm) Au (30 nm), deposited on both sides of the single crystal, by a thermal evaporator.

Time–of–flight (ToF) and energy spectrum measurement was conducted by a 1 µCi $^{241}$Am alpha particle irradiation. The time of flight technique consists of measuring the voltage transient response to the drift of carriers created by a short duration pulse of ionizing radiation. The samples have high resistivity with voltages applied on contacts such that wide high field regions can be obtained with low dc current flow. Measurement of the transit time of carriers across the high-field regions determines the drift velocity and hence the mobility.

Measurement of the amplitude of the charge pulse gives the total charge Q induced at the device contact, and hence the electron and hole mobility–lifetime products (here, only hole part was measured). The µ product values were then calculated using the single polarity Hecht equation assuming a uniform electric field inside device, $\eta = \frac{Q}{\int_{0}^{L} \frac{C(CCE)}{2d} \, dx}$, where $\eta$ is the charge collection efficiency (CCE), which was obtained from the normalized maximum voltage amplitude of charge transient spectrum, $U$ is the applied voltage, and $d$ is the detector thickness. A custom-made test fixture was used for energy-resolved measurements, connected to an ORTEC 556 bias supplement, an ORTEC 142A charge sensitive preamplifier, an ORTEC 575A shaping amplifier with an optimized shaping time of 2 µs and a standard multichannel analyzer.

Trap density was measured by admittance spectroscopy and drive-level-capacitance profiling (DLCP), which was taken under the dark and vacuum condition by using an Agilent E4980A Precision LCR Meter from 10$^{-1}$ to 10$^{3}$ Hz. The measurement temperature ranges from −50 to 10 °C. The DC bias was applied in the range of 0–40 V for MAPbI$_3$, single crystal. The amplitude of the AC bias was 20 mV for admittance spectroscopy, and in the range of 20–200 mV for the DLCP measurement. The measured capacitances at each DC bias were gathered with a homemade computer program and fitted with a polynomial function to obtain C0 and C1. The trap densities from DLCP were calculated by carrier densities at 100 Hz, and the carrier density measured at 20 kHz was regarded as free carriers since carrier freeze-out effect can be observed at a higher frequency.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

W.W. and H.M. contributed equally to this work. This work was supported by National Natural Science Foundation of China (Grant...
Conflict of Interest

The authors declare no conflict of interest.

Keywords

high carrier transport properties, perovskite single crystals, self-supply solution growth, X-ray detectors

Received: March 3, 2020
Revised: May 1, 2020
Published online: July 6, 2020
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