Solution-Grown CsPbBr$_3$ Perovskite Single Crystals for Photon Detection

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Supporting Information

Lead halide semiconductors with perovskite crystal structure and APbX$_3$ stoichiometry [A = CH$_3$NH$_3$ (methylammonium, MA$^+$), CH(NH$_2$)$_2$$^+$ (formamidinium, FA$^+$), or Cs$^+$; X = I$^-$, Br$^-$, Cl$^-$ or mixtures thereof] have recently become of perhaps the most intensely studied class of inorganic optoelectronic materials. After exhibiting unprecedented performance as solution-processed absorbers in photovoltaics with certified power conversion efficiencies presently exceeding 22%, these materials were soon also used in light-emitting diodes, lasers, ultraviolet-to-infrared photodetectors, as well as in X-ray (γ-ray) detectors. In these applications, solution- or Bridgman-grown large single crystals (SCs), thin-films or nanocrystalline forms of perovskites are utilized. Such a diversity of applications is due to the same extent due to the so-called defect-tolerance, which is lower than in monocrystalline Si, high carrier mobilities (2.5–1000 cm$^2$ V$^{-1}$ s$^{-1}$), long charge carrier lifetimes (0.08–450 µs), long electron–hole diffusion lengths (2–175 µm), and high optical absorption coefficients at the absorption edge (1–4.5 × 10$^4$ cm$^{-1}$) and high luminescence efficiencies.

The ability to grow semiconductors in the form of large SCs has always been of paramount technological and scientific importance. For instance, state-of-the-art Si solar cells are made from large SC ingots. SCs reflect, as close as possible, the intrinsic physical properties of a semiconductor and usually exhibit better electronic characteristics as compared to nanocrystalline forms of the same compound. In the case of MAPbI$_3$, for example, SCs exhibit carrier mobilities of up to 200 cm$^2$ V$^{-1}$ s$^{-1}$ (vs 0.4–40 cm$^2$ V$^{-1}$ s$^{-1}$ in thin-films) and lifetimes of up to 500 µs (vs 4.5–1000 ns in films and nanocrystals). Beyond studies of fundamental physical properties, SCs are required for the structural determination of novel compounds and for structural refinement of known materials. Perovskite SCs are notably more chemically stable than their thin-film counterparts. Recently, several solution-based approaches to growing centimeter-scale perovskite SCs have been developed. They can be divided into three categories: (i) slow crystallization upon cooling saturated aqueous hydrohalic solutions, or solutions in organic solvent, (ii) crystallization due to a change of the solvent polarity by slow antisolvent diffusion, and (iii) inverse temperature crystallization (ITC), initially proposed by Bakr et al. In the lattermost method, crystallization is caused by the inverse solubility dependence on temperature in some organic solvents and the overall growth occurs relatively fast, e.g., within several hours. Centimeter-scale SCs of all MAPbX$_3$ and FAPbX$_3$ compositions can be grown by at least one of these three approaches, enabling studies of their intrinsic electronic and optical properties, which have been reported within the last year. On the contrary, the solution-based growth of fully inorganic CsPbX$_3$ SCs remained elusive. Such all-inorganic analogs could perhaps overcome the known issues of chemical instability of hybrid perovskites. Although known since the 1950s, CsPbX$_3$ perovskites have only recently received their rightful attention in the form of thin-films and nanocrystals, demonstrating promising potential in photovoltaics and for bright light emission. Thus far, high-quality CsPbBr$_3$ and CsPbCl$_3$ SCs could only be obtained via high-temperature growth from melts using the Bridgman method (at temperatures above 600 °C, in an evacuated quartz tube, using highly pure starting reagents). In this work, we present a simple and fast route to solution growth of CsPbBr$_3$ SCs using the ITC method, under ambient atmosphere and using low-cost precursors. Obtained SCs can be handled in air and can be easily wet-polished using DMSO; all such treatments showed no substantial effect on the electric properties of SCs. We also report the sensitive detection of visible and gamma-photons as evidence of the high electronic quality of this material. We note that during the preparation of this paper, another report on solution-grown CsPbBr$_3$ SCs by Rakita et al. was published, wherein a greater focus was placed on the antisolvent diffusion method or growth from...
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Antisolvant-containing solutions at rather low temperatures. In our experiments, nucleation and growth of crystals at temperatures higher than 88 °C, at which orthorhombic-to-tetragonal phase transition takes place, resulted in crystals with improved crystallinity and different morphology.

In previous studies on hybrid perovskites, the optimal solvents for ITC growth were reported to be dimethylformamide (DMF), dimethylsulfoxide (DMSO), γ-butyrolactone and their mixtures. We find that the growth of CsPbBr3 is best carried out in dimethyl sulfoxide (DMSO). Specifically, a CsBr:PbBr2 solution (1:2 molar ratio, 1 M concentration of Pb) in a mixture of DMSO with cyclohexanol (CyOH) and DMF, was heated to 90 °C in a vial, leading to the formation of 1–3 nuclei. Subsequent heating to 110 °C led to further growth without additional nucleation. A several-mm-long, flat, orange-colored and optically clear SC was collected within several hours (Figure 1). The powder X-ray diffraction (XRD) pattern of the grounded SC (Figure 1e) is consistent with the orthorhombic modification of CsPbBr3, as previously reported.

Starting with pristine CsBr and PbBr2, and considering the known phase diagram of the Cs–Pb–Br system, there are 3 plausible products of the above synthetic approach: Cs4PbBr6, CsPbBr3 and CsPb2Br5. Figure 1a summarizes the solubility of CsBr and various CsBr:PbBr2 mixtures in DMSO and indicates the identity of any observed precipitation products upon saturation. The limiting factor is the low solubility of pristine CsBr, whereas the solubility of PbBr2 is the highest (2 M at room temperature, not indicated in Figure 1a). The addition of PbBr2 notably increases the solubility of CsBr (Figure 1a,c) due to the formation of PbBr6(2−n) complexes, where n is 3 and above, thus reducing the [Cs+] [Br−] product. In aqueous, DMF and other polar solutions, PbXn−(2−n) anions (X = Br, I) with n = 3–5 have been commonly reported. Cs4PbBr6 is observed as the single precipitation product upon saturation of 4:1 CsBr:PbBr2 solutions. For 1:1 CsBr:PbBr2, we still find Cs4PbBr6 as a primary product (with small inclusions of CsPbBr3). Only upon an increase of the PbBr2 fraction (forming 1:2 CsBr:PbBr2 solutions) is the formation of the desired CsPbBr3 product with lower coordination number favored. Intermediate CsBr:PbBr2 ratios of 1:1.2 or 1:1.5 still result in a Cs-rich precipitate. A solution with a 1:2 CsBr:PbBr2 ratio produces pure CsPbBr3 precipitate at any temperature in the range of 25–110 °C (Figure 1a). As expected, the further increase in PbBr2 concentration leads to the precipitation of CsPbBr3. The solubility of most compounds in Figure 1a is fairly independent of temperature. Only at a 1:2 ratio of CsBr:PbBr2 do we find a significant, ~40% drop in the solubility between 75 and 90 °C. At these temperatures, such a behavior resembles the rarely observed phenomenon of retrograde solubility. This phenomenon has been generally explained by the negative enthalpy of solubilization, and the corresponding temperature coefficient of the solubility is then equal to −ΔHf°/T2. Previous studies by Bakr et al. indicated the relevance of retrograde solubility to all FAPbX3 and MAPbX3 compositions in DMF, DMSO and γ-butyrolactone, and pointed to a complex interplay between the solvation of ions and complexation equilibria of PbXn−(2−n).

All compounds showed a steady decrease of solubility with increasing temperature, except for MAPbI3 where solubility increased until 60 °C and then decreased. A more complex behavior in our case, i.e. the coexistence of the temperature-independent regions below and above the rather narrow retrograde solubility region, calls for additional considerations. One important factor might be an orthorhombic-to-tetragonal phase transition, reported to occur at 88 °C in thermodynamic equilibrium. The solubilities of each phase are likely to be different, causing a transition range on a solubility-temperature profile.

Although a solubility gradient, such as the one in Figure 1a, in principle allows the growth of SCs, the particularly steep dependence for 1:2 CsBr:PbBr2 solutions in DMSO might also be problematic. Overly fast oversaturation upon heating causes the formation of multiple nuclei and/or polycrystals. We found that the solubility-temperature profile can be smoothed by the addition of CyOH or a CyOH/DMF mixture (Figure 1b). SC growth from such solvent mixtures led to better reproducibility of the results and only 1–3 crystals per vessel. These crystals nucleate at ~90 °C and continue to grow at temperatures up to 110 °C without further nucleation. The best quality SCs were obtained at an overall growth rate of below 0.2 mm/h.

Figure 1. Temperature dependence of the solubility for CsBr, Cs4PbBr6, CsPbBr3 and CsPb2Br5 in (a) DMSO and (b) a DMSO/CyOH/DMF mixture. (c) Effect of PbBr2 addition on CsBr solubility in DMSO and a DMSO/CyOH/DMF mixture. (d) Photographs of the obtained CsPbBr3 SCs. (e) Powder XRD patterns of the obtained SCs (brown) in comparison with the reported crystal structure of CsPbBr3 (ICSD card #97851).
Nucleation at 90 °C and above is critical for the formation of CsPbBr3 SCs with high optical clarity. Such SCs have rectangular, plate-like shape and behave as single crystals under polarized light (Figure 2). At growth rates higher than 0.2 mm/h, the crystals have a tendency to grow faster in one direction (such as in prism-like shapes, ~3 x 0.5 x 0.5 mm) and start appearing to have large scattering inclusions (Figure S1). Nucleation at lower temperatures leads to granular, turbid crystals, indicating polycrystallinity. Similar problems were encountered when trying alternative growth methods, e.g., via cooling of hydrohalic aqueous solutions or using slow diffusion of an ethanol-water mixture into DMSO solutions (details can be found in SI, Methods 2 and 3, respectively; photos exemplifying these crystals are shown in Figure S2). In these methods, nucleation and growth occurred at 25−70 °C.

The optical absorption spectra of CsPbBr3 SCs is evaluated using diffuse reflectance data, analyzed through the Kubelka−Munk equation, and show step-like behavior at the band edge (Figure 3a). The spectrum can be fitted with a direct-gap Tauc plot (inset in Figure 3a) yielding a bandgap energy of about 2.254 eV. A similar value of 2.25 eV was reported for Bridgman-grown CsPbBr3 SCs.12 The transparency region can be used to calculate the refractive index from the reflectivity spectrum (Figure S3). A normal dispersion of refractive index from 2.3 to 2.2 for the wavelength region of 580−800 nm was observed.

For electronic transport and photon detection measurements, we deposited electrodes of Ag paste on opposite facets of the SCs. We then tested CsPbBr3 SCs as detectors in the visible region, a 1 order of magnitude increase of the peak photocurrent due to the prevalence of bulk transport. This improvement was then fitted with a Hecht model (red line).

Efficient photoconductivity in the bulk of a SC is a prerequisite for sensing deeply penetrating X-ray and especially gamma-photons. This inspired us to test our CsPbBr3 SCs for the detection of gamma-photons. We constructed a gamma-photon counting device, as detailed in the SI and in our previous studies on hybrid MAPbI3 and FAPbI3 SCs.11 A high count rate could be detected, similar to the hybrid perovskite SCs tested under identical conditions. We then attempted to perform energy-resolved counting using standard pulse-height analysis. With moderate cooling to −53 °C (220 K), we could detect a broad photopeak from a 241Am source, not seen at room temperature (Figure 3c). We also find that the increase of bias from 20 to 40 V notably shifts the photopeak to higher channels of the same multichannel analyzer and slightly improves the energy resolution, illustrating that charge-collection efficiency remains a strongly limiting factor. For efficient collection of carriers, a high mobility-lifetime product (μτ) is crucial. Together with the applied electric field, E, one can estimate carrier drift lengths as μτE. This drift length must be at least equal to the size of the whole SC for efficient collection of photocarriers. For the evaluation of μτ within the bulk of the crystal using electronic measurement, we have investigated the bias-dependence of the photocurrent at 550 nm (Figure 3d).
product of $\sim 2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ which is slightly lower than in Bridgman-grown CsPbBr$_3$ SCs.\textsuperscript{12} Typical $\mu\tau$ values for Cd$_{1-x}$Zn$_x$Te, the present commercial room-temperature detector material, are close to $1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1}$. Similarly high values of $1-1.8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1}$ were also observed for SCs of hybrid perovskites MAPbI$_3$ and FAPbI$_3$ in our previous studies using the same measurement method.\textsuperscript{11} A smaller $\mu\tau$ product in CsPbBr$_3$ than for hybrid perovskites can be attributed to shorter carrier lifetimes. In hybrid perovskites, asymmetric organic cations form asymmetric electric fields that assist in carrier separation, increasing carrier lifetimes.\textsuperscript{52}

Furthermore, we compared the resistivity of solution-grown CsPbBr$_3$ SCs ($2 \Omega \text{ cm}$) with the best values reported for Bridgman-grown SCs ($343 \Omega \text{ cm}$).\textsuperscript{12} Such a difference suggests that solution-grown SCs might incorporate impurities acting as electronic dopants or have higher concentration of defects, thus increasing the carrier density. Further work on the exclusion of these impurities might lead to higher resistivities, and hence more closely representative intrinsic behavior, favorable for photon detection.

In summary, we have shown that transparent CsPbBr$_3$ SCs can be grown from DMSO solutions using the ITC method. Owing to the low density of traps and low carrier density, along with a moderately high carrier mobility and a high gamma-photon absorptivity due to being a heavy-metal based compound, a high sensitivity to gamma-irradiation can be demonstrated. We find that higher doping levels from impurities, as compared to Bridgman-grown SCs, still limits the energy resolution of gamma-counting. Further optimization of the proposed synthetic protocol may concern increasing the purity to reduce the doping level and also surface engineering to decrease the density of traps.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b04298.

Synthetic and characterization details, photos of CsPbBr$_3$ crystals, refractive index (PDF)

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**Author Contributions**

The paper was written through contributions of all authors.

**Notes**

The authors declare no competing financial interest.

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