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Single-Crystal-Like Optoelectronic-Properties of MAPbI₃ Perovskite Polycrystalline Thin Films

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Our understanding of the crystallization process of hybrid halide perovskites has propelled the efficiency of state-of-the-art devices to over 22 %. Further improvements to the performance will likely arise from reducing the number of grain boundaries. Here, current methods lead to grain sizes in the 1-micrometer range and the resulting optoelectronic properties suffer as compared to single-crystal materials. In this work, we introduce a new synthesis procedure with MAPbI₃ leading to crystal sizes in the tens of microns range. This approach is based on the pre-crystallization of an intermediate phase (IP) based on the solid-state reaction of a lead-acetate trihydrate precursor mixture in a highly polar solvent. Beyond large grain sizes, the crystal orientation is also tightly controlled, leading to perovskite crystallites which remain perfectly aligned with the c-axis of the tetragonal structure parallel to the substrate as evidenced by grazing incidence wide angle X-ray scattering (GIWAXS). Furthermore, we demonstrate the high crystallinity and large grain size of the developed films via high-resolution transmission electron microscopy (HRTEM). The charge carrier mobilities are significantly improved with larger grain size and approach mobility values of about 40 cm²/Vs, moving toward the values observed for single crystals. We capitalize on the enhanced optoelectronic properties of the developed films by incorporating them into planar heterojunction solar cells which reach power conversion efficiencies of 18.5 %, higher than MAPbI₃-based device prepared from standard methods in a like-to-like comparison.

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Introduction

Hybrid halide perovskite materials have galvanized the optoelectronic community due to their unprecedented easy and low-cost fabrication combined with remarkable optoelectronic properties, reminiscent of GaAs.^{1, 2} Polycrystalline perovskite-based photovoltaic devices already reach efficiencies above 22 % after extensive optimization of the perovskite film morphology and composition and engineering of the film interfaces.³⁻⁶ However, the density of grain boundaries in those polycrystalline perovskite films is still rather high, which places a constraint on the charge transport properties of the perovskite films and ultimately will limit the maximum achievable device performance.⁷

Single crystals of perovskite materials show a dramatic improvement of all optoelectronic properties, including charge carrier mobility, charge carrier diffusion length, and a substantially reduced defect density.⁸⁻¹¹ Therefore, a higher performance can be expected with single crystalline perovskite absorber layers, as is the case for Si- or GaAs-based photovoltaic devices.¹² However, the growth of single crystalline thin perovskite films is challenging¹³⁻¹⁵ and the forced lateral architecture with sequentially deposited electrodes, charge extraction material and buffer layers. Such devices to date do not show competitive efficiencies.^{13, 16} Instead, the main improvement to perovskite solar cells has risen as a result of the development of novel synthesis methods focussing on polycrystalline films with vertical device stack architectures.^{3, 17} Nevertheless, in order to facilitate further progress in the performance of perovskite solar cells, we must tap into the full potential of perovskite materials by targeting thin films that exhibit properties similar to those of single crystals, i.e. macroscopic crystal grains and minimum disorder at the grain boundaries.

To this end, a precise control of orientation and morphology of polycrystalline films will be necessary. Currently, a plethora of deposition methods are being developed and studied for the methylammonium lead iodide (MAPbI₃) compound. In particular, the crystallization kinetics and dynamics were investigated with different lead(II)-precursors and different methylammonium iodide (MAI) ratios¹⁸⁻²¹ or different solvents for the precursor solution, in both one and two-step approaches.²²⁻²⁷ In general, the crystallization kinetics can be divided into three categories: (i) direct formation of the perovskite material from a precursor solution mixture, (ii) sequential addition of the perovskite components or (iii) formation of an intermediate crystalline or amorphous phase which is then converted into the perovskite phase. Employing the first method leads to little control of the morphology, albeit rather large crystals can be formed if an ionic liquid or the anti-solvent technique is used.^{28, 29} Employing a sequential deposition approach (ii) generally leads to small grain sizes in the range of hundreds of nanometers.³⁰ The formation of an intermediate phase (iii), especially the Pb-Dimethylsulfoxide (DMSO) complex³ so far resulted in perovskite films showing highest efficiencies in perovskite solar cells. However, the intermediate phase is

formed from solution and is highly unstable.³¹ Therefore, this approach usually lacks fine control of perovskite formation and does not lead to perovskite grain sizes exceeding 1 μm .^{3, 22-24, 32}

Larger grain sizes have been already reached for MAPbBr₃ based thin films in our previous work based on the use of the lead acetate precursor.³³ Grain sizes larger than 10 μm were achieved in a smooth thin film comprising perfectly aligned crystals with respect to the substrate. For MAPbI₃ films, so far only crystal sizes in the nanometer range were synthesized with the use of the lead acetate precursor. However, two independent studies showed that if using the PbAc₂ precursor, the amount of hydration water during perovskite synthesis is essential for optimized photovoltaic performance of the employed perovskite films in devices.^{34, 35} Thus, the role of the hydration water for the perovskite synthesis needs to be understood to further improve this synthesis strategy. In this paper, we introduce a new crystallization strategy based on lead acetate trihydrate. Dissolving this precursor mixture in a highly polar solvent, such as tetrahydrothiophene 1-oxide, leads to the formation of an air-stable intermediate phase that can be converted into the perovskite phase upon heating. We controlled the crystallization process by reducing the nucleation rate significantly and triggering fast perovskite growth with the annealing step, leading to grain sizes of over 10 μm in a homogeneous thin film. This increase in grain size and orientation leads to remarkably enhanced optoelectronic properties of the polycrystalline perovskite films reaching single-crystalline properties, such as charge carrier mobility values in the range of 40 cm²/Vs. When introduced into devices, solar cells based on the new approach resulted in power conversion efficiency values above 18.5 %, significantly above those found for traditional approaches in a like-to-like comparison.

Results and discussion

The MAPbI₃ thin films developed in this work are based on a new synthetic protocol using lead acetate trihydrate in combination with a highly polar solvent, tetrahydrothiophene 1-oxide (THTO). Briefly, the solid precursors are mixed in the solid form and then the solvent mixture Dimethylformamide (DMF)/ THTO is added. To form the MAPbI₃ films the solution was spin-coated at 5000 rpm for 180 s on top of the substrate and annealed at 130 °C for 5 min (see the experimental section for all details).

The crucial step in the film formation process is mixing the precursor in the solid state prior to adding the solvent mixture. As shown in Figure 1a, the colorless precursor mixture becomes yellow after manually shaking the vial. This leads to the formation of a highly crystalline intermediate phase (IP) with the crystal structure shown in Figure 1b. In the XRD pattern of the new phase, we see no presence of the precursor phases, indicating a phase-pure new compound that can be indexed to an orthorhombic structure with a

Figure 1. a) photos of the precursor mixtures before and after shaking of the vial; b) Comparison of the precursors MAI and (hydrated) $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ with resulting new intermediate phase (IP) compound from mixing both solids; c) SEM image of the needle shaped crystals from the IP; d) Schematic illustration of the spin-coating process; e) *in situ* XRD while annealing the substrate with the spin-coated precursor solution.

space group similar to P222 with lattice parameters $a=6.4 \text{ \AA}$, $b=15.935 \text{ \AA}$, and $c=27.805 \text{ \AA}$. We note that the formation of the intermediate phase relies on the presence of hydration water in the lead acetate precursor. The XRD analysis in Supporting Information (SI) of the precursor mixture using dehydrated PbAc_2 shows that no new phase is formed (cf. Figure S1a). This is not unexpected, as different researchers found hydration water in the lead acetate precursor to be necessary to crystallize high-performing perovskite films in photovoltaic devices.^{34, 35}

To further study this new IP and its structure we crystallized it from water. We found that the crystals growth is anisotropic with very long lengths in the mm range but widths in nm range as shown in Figure 1c and in the Supporting Information (Figure S1d). Our 2D XRD data show similarity to an $(\text{MA}^+)_2(\text{PbI}_3)_2 \cdot 2\text{DMSO}$ phase from a synthesis via a polymeric plumbate(II) fiber identified by Guo et al.³¹ We note that this approach can also be used for bromide instead iodide, as shown in the Supporting Information. In contrast to the Pb-DMSO complex, the IP shown here is very stable at

ambient conditions and directly converts to the perovskite phase if heated to at least 80 $^\circ\text{C}$.

To deposit the IP from the solution the choice of solvent is highly important. The most commonly used solvents such as DMF or γ -butyrolactone (GBL) do not favor the formation of the IP^{18, 34, 36} but instead result in fast perovskite crystallization, as can be seen in Figure S2a.²¹ Therefore, the

Figure 2. SEM images of perovskite films prepared from different THTO concentrations: a) 7 vol% THTO; b) 10 vol% THTO; c) 13 vol% THTO; d) 26 vol% THTO.

solvent mixture needs to be modified to promote the crystallization of the IP rather than the perovskite phase. This is achieved by simply increasing the solubility of the perovskite compared to the solubility of the IP. Foley et al. predicted with Mayer bond order calculations a slightly more negative enthalpy of perovskite solvation for DMSO compared to DMF and a much more negative enthalpy of solvation for THTO.²⁷

To find a suitable solvent mixture, we studied the crystallization behavior from a range of solvents via *in-situ* XRD measurements at ambient conditions right after spin-coating the films in a nitrogen-filled glovebox. DMF-based solutions lead to a highly crystalline perovskite phase immediately after spin-coating. However a weak reflection at around 9.6° , 2θ indicates the presence of a second phase which agrees with the IP. Employing DMSO, as shown in Figure S2b, leads to slower perovskite crystallization and a higher amount of the intermediate phase. Here, increasing the DMSO concentration leads to a competition of the lead-DMSO complex (as shown in Supporting Information) and therefore inhibited crystallization of the new IP. Finally, THTO does not form any additional intermediate phases from the perovskite precursor solution and small concentrations around 10–13 vol% are already sufficient to prevent perovskite nucleation before the IP is fully crystallized (see Figure S2c–f). In Figure 2d a schematic illustration of the final synthesis process through the IP phase is illustrated.

The *in-situ* XRD data collected in Figure 1e clearly shows the direct transformation of the (003) reflection of the IP to the (200) reflection of the perovskite. Initially, the IP shows the (003) reflection at 10° , which shifts to 9.6° upon complete drying as shown in the Supporting Information. At this stage, the IP is completely stable under ambient conditions with the same structure as from solid state reaction from the precursors. We note that the IP in the film is highly oriented and therefore mainly the reflection at 9.6° is visible. To confirm that the IP is the same in both cases, we have compared the XRD between powder from the precursor mixture and powder scraped off from the film, showing the same crystallographic pattern (see Figure S1b).

To inhibit the perovskite nucleation and promote the crystallization of the IP from solution, the addition of THTO to the solvent mixture is crucial. This, in turn, influences the resulting grain size by determining the number of potential nucleation points for perovskite phase conversion as shown in Figure 2. Grain sizes of up to $100\ \mu\text{m}$ can be reached with 26 vol% THTO additive but the films show poor grain interconnection and smoothness. We found the best compromise between grain size and total film quality to be reached with perovskite films obtained from 13 vol% THTO. This mixture leads to grain sizes of above $10\ \mu\text{m}$ in a very dense and smooth film when annealed at 130°C . Somewhat surprisingly, lower annealing temperatures and longer conversion times lead to smaller crystallites as shown in the Supporting Information.

To obtain more insights regarding crystal orientation we performed grazing-incidence wide-angle X-ray scattering GIWAXS measurements, see Figure 3a. GIWAXS is a powerful method for evaluation of crystal orientation in thin films due to the high statistical relevance and the possibility to extract quantitative information about the crystal part of the

Figure 3. a) 2D GIWAXS pattern of a samples prepared from 13 vol% THTO solvent additive to the precursor solution shown in q_x - q_y representation (a) and with total q vector vs. the polar angle (b); b) TEM cross-section of the lamella incorporating a MAPbI₃ film deposited from 13 vol% THTO; c-f) HRTEM's and their FFT's from the spots marked in b).

sample.^{37–39} A typical sample based on lead acetate and

employing DMF solvent usually shows no preferential orientation as shown in literature and in the Supporting Information for films prepared under our synthesis conditions.^{35,36,40} As shown earlier by Foley et al. the solvent THTO, on the other hand, can be used to achieve a high degree of orientation in MAPi films.²⁷ They argue that homogeneous nucleation is suppressed and instead heterogeneous nucleation starting at the substrate is responsible for this orientation. Here the synthesis parameters are different since the perovskite is formed through an intermediate phase.

However, with increased THTO concentration, the perovskite crystal alignment within the film is confined to the (200) facet parallel to the substrate as explained in the following: Figure 3a shows the 2D GIWAXS pattern of a film with 13 vol% THTO. The strong preferential orientation of the MAPbI₃ crystallites is apparent from the individual scattering reflections which are labeled according to the crystal planes from which they originate. The splitting of the cubic (110) and (111) peaks gives rise to the (112)/(200) and the (211)/(202) pair of peaks, respectively, and shows that the sample is in the tetragonal phase. In comparison, in the 2D GIWAXS pattern of the sample prepared from pure DMF solvent the reflections adopt the form of Debye-Scherrer rings indicating no preferential crystal orientation (cf. Figure S4c).

statistically. Therefore, the peaks were fitted with Voigt functions and their position was determined to be $44.8(3)^\circ$. These peak positions verify that the sample is oriented with the (200) facet parallel to the substrate which can be imagined as a cuboid lying on its side. The extremely narrow FWHM of $2.0(7)^\circ$ of these Voigt functions shows how well the MAPbI₃ crystals are aligned inside the film. As seen in Figure S5, already 10 vol% of THTO additive is sufficient for strong crystal alignment and 13 vol% THTO is optimal for pure crystal alignment verifying the GIWAXS result. However, with increased THTO concentration, the perovskite crystal alignment within the film is confined to the (200) facet parallel to the substrate.

As seen in Figure S4 and S5, already 10 vol% of THTO additive is sufficient for strong crystal alignment and 13 vol% THTO is optimal for pure crystal alignment. The strong preferential orientation of the MAPbI₃ crystallites is apparent from the individual scattering reflections which are labeled according to the crystal planes from which they originate. The splitting of the cubic (110) and (111) peaks gives rise to the (112)/(200) and the (211)/(202) pair of peaks, respectively, and shows that the sample is in the tetragonal phase. Here, the peak positions seen in GIWAXS verify that the sample is oriented with the [200] vector perpendicular to the substrate. This can be imagined as a cuboid lying on its side.

Figure 42. a) representative transients obtained at 42 μm spacing; b) Extracted transit times for holes from ToF with perovskite films deposited from different THTO concentrations; c-f) device performance deviation of devices in the architecture $\text{FTO}/\text{TiO}_2/\text{Cs}_2\text{O}_3/\text{MAPbI}_3/\text{Spiro-OMeTAD}/\text{Au}$ employing perovskite films deposited from different THTO concentrations.

Azimuthal line cuts around the q range of the (002)/(110) and their second order peaks (004)/(220) of the 13 vol% THTO data are plotted with intensity vs. azimuthal angle γ in Figure S4b. From the intensity distribution in these cuts, the orientation of crystals in the film can be evaluated

Polar cuts around the q range of the (002)/(110) and their second order peaks are plotted in Figure S4. The peaks were fitted with a Voigt function and their position was determined to be $44.8(3)^\circ$. The peak positions seen in GIWAXS verify that the sample is oriented with the [200] vector

perpendicular to the substrate. This can be imagined as a cuboid lying on its side, with an extremely narrow FWHM of $2.0(7)^{\circ}$ which shows how well the MAPbI₃ crystals are aligned inside the film.

To determine the actual grain size within the perovskite film we performed high resolution transmission electron microscopy (HRTEM) on a cross-section of a photovoltaic device. To this end, we cut a 45 μm long lamella with a focused ion beam from a complete solar cell device in FTO/TiO₂/MAPbI₃/Spiro-OMeTAD/Au architecture (see the Supplementary Information for the full analysis). In Figure 3 we show a representative area of a 16 μm long TEM cross-section. Here, HRTEM images from four different spots are shown together with their fast Fourier transform (FFT). A change in pattern can only be observed at bright regions between the grains. Thus, we assume the bright lines to be the grain boundaries. In the image, the FFT pattern along the 12 μm distance between the bright areas does not change, indicating that it is indeed a single crystal. Our results show that there are only mainly two distinct crystal orientations in the in-plane direction in this sample, confirming the high degree of order in the material. We note that the samples are highly sensitive to the electron beam and particularly the grain boundaries become broader with longer illumination times.

To additionally classify the different layers in the cross-section, we performed energy-dispersive X-ray spectroscopy (EDX) during the TEM investigation, as shown in Figure S7. Here, we can clearly distinguish between our different layers in the stack with the distribution of different atoms present and detectable. We see no heterogeneity in our perovskite layer, confirming their high quality.

Table 1: Extracted mobility values from ToF measurement showing increasing charge mobility with grain size. The 26 vol% sample (*) was measured with a different procedure as discussed in the Supporting Information.

THTO conc. / vol%	Hole mobility / cm ² (Vs) ⁻¹	Electron mobility / cm ² (Vs) ⁻¹	Stand. Dev.	Sum / cm ² (Vs) ⁻¹
0	8	9	1	17
7	11	12	1	23
10	13	13	1	26
13	15	17	1	32
26*	17*	23*		40*

To quantify the improvement in optoelectronic properties with larger grains in our polycrystalline films we performed Time of Flight (ToF) measurements as shown in Figure 4. ToF measurements were performed in a lateral sample configuration where the different MAPbI₃ films were deposited on top of an in-plane gold contact pattern. The different electrode spacing d in the range of several tens of micrometers allow for photocurrent measurements at

different charge carrier distances before being extracted at the opposite electrode. Charge carrier generation is induced upon pulsed laser excitation at the margin of one contact while drift of the charges occurs due to an external DC field ($E = 5 \text{ kV/cm}$) which is applied only during the short measurement period of the j - t profile. Since the charges are created locally near one electrode, the polarity of the E-field defines whether electron or hole transport across the material is observed. A detailed description of the employed setup can be found in the Supporting Information.

Representative transients obtained for different electrode spacings are shown in Figure 4b. Following a fitting procedure for ToF transients⁴¹, the transit time t_{tr} was extracted and plotted as a function of d for every investigated material (Figure 4a). Because of the linear dependence of t_{tr} on d , the mobility can be calculated from the respective fit according to $\mu = d/(E \cdot t_{tr})$. The determined values are listed in Table 1. Clearly, an influence of the grain size is observable.

With increasing grain size the mobility values increase, indicating improved transport properties due to a reduced number of grain boundaries which represent potential recombination sites.⁷ We note that a full analysis of the 26 vol% THTO sample was not possible due to a large number of pinholes in the film. Therefore, the photocurrent in this device was only measurable for a small amount of different electrode spacings with no representative trend from the obtained transients. The value presented here was obtained from a voltage series performed on a fixed gap size where the photocurrent was detectable (see Figure S8) and represents a lower limit of the mobility. We further note that the measurement of lateral configuration is essential to gain information on the optoelectronic properties of the perovskite layer, while vertical in-plane devices show several limitations for data acquisition.⁴² Additionally, our sample configuration allows for the measurement of charge transport on a macroscopic scale over several micrometers reflecting the influence of grain boundaries and defects, thus directly affecting the charge transport. Although the charge transport in the photovoltaic device will be across and not along the film thickness, a reduced number of recombination sites like defects in the film is beneficial for efficient charge extraction.

In order to study the effect of crystal size on device performance, we prepared devices in a planar heterojunction configuration (FTO/TiO₂/C₆₀/Al₂O₃/MAPbI₃/Spiro-OMeTAD/Au). We show a box plot distribution of the device performance of at least 8 devices for the different perovskite films in Figure 4. Here, we mainly observe an increase in fill factor (FF), correlating with the improved optoelectronic properties of the bigger crystal films. We note that for devices fabricated from films with crystal sizes above 3 μm (namely 10 vol% and 13 vol% THTO) no significant difference in device performance occurs. The performance of these two samples is in fact within the experimental error of the system and show the highest value at 18.5 % as well as the highest reproducibility. Here, we mainly observe an increase in fill factor (FF) with smaller variations for grain sizes larger than

2 μm (namely 10 vol% and 13 vol% THIO). These samples also show the highest performance at 18.5 % and the highest reproducibility. The high currents above 22 mA/cm^2 , which are gained in these devices correlate perfectly with the integrated current from EQE measurement with 22.45 mA/cm^2 (see Figure S9). However, all the devices employing architectures as shown in Figure 4 have high hysteresis with non-stabilized power output. This instability is mainly related due to the charge extraction material and not the perovskite layer, since with devices employing Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) or [6,6]-Phenyl C_{60} butyric acid methyl ester (PCBM) minimal hysteresis and stabilized power output can be obtained (see Figure S9).

The perovskite films with the largest grain sizes contain a large number of pinholes which leads to semi-transparent films with an average transmittance of about 28 % in the visible range, as shown in the Supporting Information. Therefore the device properties drop if these films are incorporated. However, the current in these devices is extremely high with 19 mA/cm^2 on average which is much higher than for any reported semitransparent MAPbI_3 -based solar cells with a transmittance of about 20-30%.⁴³⁻⁴⁶ Therefore, the device efficiency reaches very high values with the maximum at 12 %, which is 4 % higher than that of devices shown in the literature with semitransparent appearance due to pinholes.⁴³

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Conclusions

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We have demonstrated a new route to deposit hybrid perovskite films with extremely large and perfectly oriented crystallites of 10–40 μm in size. In order to achieve this, we targeted a new, highly stable intermediate phase based on lead acetate trihydrate. Importantly, we find that a highly polar solvent, such as tetrahydrothiophene 1-oxide is necessary to inhibit the perovskite phase growth and to favor the crystallization of the IP. With HRTEM we can clearly identify the grain boundaries and verify high crystallinity and order within the perovskite film. The newly developed films show optoelectronic properties similar to those found in perovskite single crystals with very high mobility values in the 40 cm^2/Vs range. We capitalized on these improved properties by fabricating solar cells with a planar heterojunction architecture. The highly oriented and large grains lead to a power conversion efficiency of 18.5 %, higher than what is achieved with standard fabrication in a like-to-like comparison.

Conflicts of interest

There are no conflicts to declare.

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