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Grain boundaries act as solid walls for charge carriers in large crystal MAPI thin films

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Abstract

We studied single crystalline MAPI thin films using time-resolved PL microscopy and numerical model calculations. Diffusive transport inside the material leads to a time lagged PL emission peak for increasing distances between the position of excitation and detection. From the measured time delay and the distance, the diffusion constant can directly be determined. Vertical grain boundaries in the film were found to act as solid barriers, restricting the diffusive carrier transport. Compared to the unrestricted case in large crystals, this results in brighter and longer-lived PL in regions close to grain boundaries and edges, which is well reproduced by theoretical model calculations. Our experimental results show no quenching or additional loss channels due to grain boundaries for the studied material.

Keywords

Perovskites, Solar Cells, Thin Films, Hybrid Materials, Photoluminescence, Restricted Diffusion, Charge Transport, Hole Transporting Material

Organic-inorganic metal halide perovskites have developed into promising candidates for next-generation solar cell technology.^{1,2} Extremely fast progress in this field has taken cell efficiencies from 10% in 2012³ to 20% in 2015⁴ to a current maximum of 22.1%⁵ – already approaching the quality of silicon^{5,6} or copper indium gallium selenide (CIGS)^{5,7} thin film solar cells. Since the fabrication is compatible with solution-processing techniques and the employed materials are cheap and readily available a large variety of material compositions, preparation techniques and device structures has been developed within the past few years.^{8–13}

One of the most intensively studied organic-inorganic metal halide perovskites is methylammonium lead iodide (MAPI) which forms the basis of perovskite-based solar cells with highest efficiencies. For MAPI efficient and long-ranged charge carrier diffusion has been reported reaching up to $65\mu\text{m}$ in the case of single crystals and $10\mu\text{m}$ in nanocrystalline thin films, respectively.^{2,14–16} Closely connected to the diffusion length is the lifetime of created charge carriers, which typically lies in the microsecond range and is unusual for a direct bandgap semiconductor.¹⁷ The direct consequence of these single crystals properties is that grain boundaries will have a significant impact on the overall performance of polycrystalline solar cell devices. For single crystal thin film solar cells without grain boundaries in the vertical direction, these effects might be smaller. But a detailed understanding of the underlying physics is nevertheless important if non-microscopic characterization methods like PL, time-of-flight, microwave conductivity and others are used, which would usually average over areas of tens of microns. The same holds for lateral measurements, where grain boundaries would always influence the transport. The central questions, which we will cover here, are if the boundaries act as quenching sites, if they allow charge carriers to pass, or if they should be seen as solid walls?

Charge carrier dynamics and diffusion in perovskite materials have been studied using different techniques including time-resolved microwave conductivity, pump-probe and time-resolved photoluminescence.^{15,16,18–23} The latter two techniques were also combined with confocal microscopy providing information on the sample homogeneity. In addition, focused excitation and remote detection have been used to directly visualize carrier transport. Radiative transport of photoluminescence light guided in thin MAPI films (100 nm) was found to promote photon recycling at large distances.^{21,22} For solution grown MAPI crystallites with a size of several microns, long-ranged diffusive charge carrier was observed from which the diffusion constant of the material could be determined.¹⁵ These studies indicated that the PL dynamics have to be disentangled from the charge carrier dynamics in order to determine the PL decay times.²³ The role of crystal boundaries in MAPI has been studied both theoretically and experimentally. Time-domain atomistic simulations indicate that they can accelerate electron-hole recombination in polycrystalline MAPI thin films by enhancing electron-phonon coupling²⁴ while first-principle calculations suggested them to be rather benign.²⁵ Cathodoluminescence experiments on individual sub-diffraction grains revealed highest variability in the luminescence intensity at the exposed grain surfaces, which was attributed to surface defects.²⁶ Correlated confocal fluorescence and scanning electron microscopy studies on Chlorine-treated MAPI thin films showed that carrier lifetimes varied widely for different grains while grain boundaries appeared dimmer with faster non-radiative decay.²⁷ More continuous films then were found to show longer lifetimes.²⁸ A recent study on individual microcrystallites using fluorescence lifetime microscopy suggested that grain boundaries are impervious to charge carriers and do not enhance non-radiative recombination.²⁹

In this manuscript we report on the charge carrier diffusion and energy transport and the role of grain boundaries in single-crystalline MAPI thin films fabricated following our lead-acetate precursor route³⁰ including the new solvent additive tetrahydrothiophene 1-oxide (THTO) suggested by Foley et al.³¹ The material is highly crystalline with the long

c-axis oriented parallel to the substrate and therefore constitutes a model system to separate bulk and boundary effects. For details on the sample preparation and characterization refer to the supporting information, section 2. This material, termed THTO-MAPI, achieves an average power conversion efficiency (PCE) of 18 % when embedded in a planar device configuration. Using time-resolved confocal photoluminescence microscopy and detection beam scanning for fixed excitation positions we first identify the different contributions to the observed PL signal and determine the charge carrier diffusion constant. We then show that the grain boundaries in these films act as hard walls restricting charge carrier diffusion to the illuminated single crystal within the film. Given the complex and random shape of the individual grains in the context of the thin films, it was necessary to build a numerical model that is able to cover the exact shape of the observed sample regions. Aided by such calculations we show that this spatially restricted diffusion strongly affects the observed PL characteristics leading to an apparent slow down of the initial decay at grain boundaries.

Figure 1: (a) Scanning electron micrograph of a THTO-MAPI thin film showing a continuous arrangement of large single crystals with sizes in the ten micrometer range. The individual crystals are separated by clearly visible grain boundaries. (b) Schematic of the experiments: Confocal images are recorded by raster-scanning the sample with overlapping excitation and detection position. Detection beam scans are obtained after local excitation at a fixed position while scanning the detection point d . PL from diffusing charge carriers is detected as a function of position x, y (distance d) and time-delay t .

Figure 1(a) shows a scanning electron microscopy image of a typical THTO-MAPI film.

The film consist of large single crystals with sizes of up to several tens of micrometers. The crystallinity of the sample, which is homogeneous in the vertical dimension, has been confirmed by x-ray diffraction measurements, see supporting information Figure S3. The individual crystals are separated by clearly visible grain boundaries, which appear dark, which also indicates that they are no efficient scatterers.²⁷ In this paper we studied the transport of photo-created charge carriers utilizing a contactless approach illustrated in Figure 1(b). By focused excitation using a picosecond pulsed diode laser (635 nm / 1.95 eV), a localized charge carrier distribution is created. In the following, these electrons and holes will undergo diffusion and finally recombine, emitting photoluminescence (PL) light at a wavelength of around 775 nm (1.6 eV). This PL of the film is detected as a function of distance d between excitation and detection and time t with a resolution of 300 nm and 1 ns respectively (for details refer to the supporting information, section 1). Due to the separation of excitation and detection in combination of the high spatial and temporal resolution, we are able to do a detailed investigation of the PL dynamics in time and space. Because the diffusion length is typically tens of microns in MAPI thin films,² the diffusion dynamics can be mapped with little spatial averaging, which allows to directly see the influence of grain boundaries.

We first investigated large crystals within the film for which the grain boundaries are expected to play a minor role and to identify the origin of the detected PL contributions. A representative confocal PL image of a THTO-MAPI thin film is shown in Figure 2(a). A large single crystal is seen surrounded by other crystals for which highlighted the grain boundary by a white dashed line. Figure 2(b) displays the detection beam image for this crystal upon focused excitation at its center. While strongest emission is observed at the excitation point, PL is also observed for larger distances. Remarkably, the ground boundaries can be clearly identified in this image indicating that efficient transport is limited to the area inside the illuminated crystal.

In Figure 3(a) we present a series of PL transients recorded for increasing excitation-detection distance d along the line, indicated in Figure 3(b). The transient detected at

Figure 2: (a) PL scan image of a THTO-MAPI thin film. (b) Detection beam PL scan of the same area recorded up to focused excitation of the large crystal in the center. PL is detected within the illuminated crystal reflecting long-ranged charge carrier and / or energy transfer. The clearly visible grain boundaries and the weaker PL in neighbouring crystal indicate substantially reduced transfer between crystals.

the excitation point ($d = 0$) features a rapidly decaying curve (red line). For increasing distance an additional, delayed component is observed which is shifted to longer times for larger distances indicated by the increasing delay time Δt between the initial peak and the maximum of the delayed component. Notice that the initial peak occurs always at time zero, regardless of the distance from the localized excitation point. Not shown in the normalized plots is the fact that its amplitude decreases with increasing distance, a trend that will be discussed below. Figure 3(c) shows a false color plot of PL transients normalized to their respective peak intensity for varying distances d that illustrate the two signal components.

The distance dependent transients can be modelled by 2D charge carrier diffusion and radiative transport within the thin film. The latter results from the higher refractive index of the perovskite as compared to the glass substrate and the PMMA used to protect the film from degradation due to moisture. Up to now, no model was reported in the literature that can quantitatively describe both features in the transients.

The recent “standard model” in the literature³² describes the charge carrier concentration

Figure 3: (a) PL transients (red lines) detected at the excitation point $d = 0 \mu\text{m}$ and at increasing distances at $d = 2.6 \mu\text{m}$ and $d = 3.8 \mu\text{m}$, respectively. The additional delayed peak, shifting to longer times Δt results from charge carrier diffusion. The peak at $t = 0$ is due to radiative transport of the PL light within the film. The blue lines are model curves, sharing a common parameter set and a diffusion constant of $D = 1 \text{ cm}^2/\text{s}$. (b) Confocal PL image of the measured crystal, indicating the excitation (x) and measurement positions (line). (c) False color plots of the measured PL transients for varying excitation-detection distances d together with the simulation results in (d).

dynamics by means of the following partial differential equation:

$$\frac{\partial n}{\partial t} = D\nabla^2 n + G - k_3 n^3 - k_2 n^2 - k_1 n, \quad (1)$$

where G is a time and position dependent charge carrier generation rate, reflecting the laser excitation, k_3 accounts for Auger recombination, k_2 reflects the radiating bi-molecular recombination rate constant of free electrons and holes, and k_1 is the non-radiative mono-molecular charge recombination rate. The assumptions made in Equation 1 are that the

material is undoped, i.e. the concentrations of electrons and holes are similar $n_e = n_h = n$, and that they share a common diffusion constant which is spatially uniform $D_e = D_h = D$.

PL emission at a point $\vec{r}$ and time t is therefore proportional to $k_2 n^2$ and only depends on the local carrier concentration $n(\vec{r}, t)$. To model the present experimental data at early times, we can neglect all three decay channels (k_1, k_2, k_3), because the estimated peak charge carrier density of $3.2 \times 10^{17}/\text{cm}^3$ lies in a regime where the total losses during the initial 200 ns are negligible (see supporting information section 3 for a reasoned estimation). The analytical solution to the diffusion problem for delta-peak excitation in two dimensions reads:

$$n(d, t) = N_0 \frac{1}{4\pi D t h} \exp\left[\frac{-d^2}{4Dt}\right]. \quad (2)$$

Here N_0 is the initial number of laser generated charge carriers at time zero, d is the distance from this laser excitation, and h is the sample film thickness, 300 nm in our case.

The directly emitted PL is then calculated proportional to $n^2(d, t)$:

$$I_{direct}(d, t) = \eta \cdot n^2(d, t), \quad (3)$$

where η accounts for the quantum efficiency, radiative rate and detection sensitivity.

The contribution of radiative transport at time zero is a well known effect in thin film solar cells.^{21,33} Due to total internal reflection, any locally created light emission at angles larger than the critical angle will remain inside the film. This waveguided PL will be scattered out towards the detector due to film roughness and defects. It is modelled here according to Lambert-Beer's law by an exponential decay function together with a $1/d$ reduction, accounting for the 2D case, which is spatially convoluted with the source I_{direct} ¹:

$$I_{guided} = \theta \cdot I_{direct} * \frac{\exp(-d/\sigma)}{d}, \quad (4)$$

¹The convolution is well defined in the 2D case where $d = \sqrt{x^2 + y^2}$, even though $1/d$ diverges at point zero.

where σ describes the extinction of the PL propagating within the crystal due to scattering and absorption and $(*)$ denotes the spatial convolution. Due to the fact that we are dealing with thin films, there are numerous scattering sites on the top and bottom surface of the film, leading to a more pronounced radiative peak in the transients as compared to studies with much smoother nanowires and nanoplates of the same material.¹⁵ θ is an amplitude factor, accounting for the scattering efficiency and detection sensitivity.

To include the diffraction limited laser excitation focus, we spatially convolute eqn. 2 and eqn. 4 with the point spread function of the microscope setup³⁴ which we approximate using a Gaussian line-shape function with a width (FWHM) of 230 nm. For the detection, we repeat this, using a FWHM of 300 nm. Finally, the two contributions are summed up and temporally convoluted with the instrument response function, modelled by a Gaussian function with a FWHM of 1 ns.

The blue curves in Figure 3a) and the full simulation in Figure 3d) present the result of this approach, describing the measured data very well. The parameters used here were determined by a fit to the data, which yields a diffusion constant of $D = 1.0 \text{ cm}^2/\text{s}$, corresponding to a charge carrier mobility of $\mu = 40 \text{ cm}^2/\text{Vs}$, and a scattering length of $\sigma = 1.2 \mu\text{m}$. This value is in agreement with the experimentally observed exponential decay of the PL at early times as determined from time-resolved confocal PL scans (Figure S7 in supporting info). Importantly, this value is about one order of magnitude larger than the absorption length of light at the excitation wavelength supporting the notion that the initial PL peak observed for increasing distances d is due to waveguided PL inside the crystal. A simpler method to determine the diffusion constant is to find the maximum of eq. 2 and solve it for D at a specific position d :

$$D = \frac{d^2}{4 \cdot \Delta t}. \quad (5)$$

The determination of the diffusion constant from the distance between initial and delayed peak is robust with respect to variations of the exact shape of the transient, but not as accurate. The initial decay at $d = 0$ reflects fast carrier diffusion and cannot be used to

determine the excited state or carrier lifetime.

So far, the discussion was based on the assumption of unrestricted diffusion and the described model would be applicable to large, quasi infinitely extended crystal. In the following, we study the role of grain boundaries for charge carriers, as they can have a major influence on charge carrier transport through a film.

In Figure 4 we chose a sample area with a smaller ($10\mu\text{m}$) crystal. In the confocal PL scan with synchronized excitation and detection spot in Figure 4(a) we note a general tendency of smaller grains appearing brighter than larger ones, which is observed also for other areas. Figure 4(b), shows a detection beam scan recorded upon focused excitation of the central crystal inside a sharp corner at position *A*. The strongest signal stems from the excitation site accompanied by a sizable signal from all over the crystal. Time-resolved detection beam scans shown in Figure 4(c) reveal that the initial charge carrier population, created by the laser, is spreading out to the entire crystal within about 200 ns. Individual transients at different positions *A* and *B* demonstrate again the presence of a delayed rise and a sharp peak at time zero, shown in Figure 4(d). After these initial 200 ns, the PL transients inside the crystal feature the same monoexponential decay with time constant of $2.5\mu\text{s}$ indicating that the spatial distribution of charge carrier has reached a steady state (see supporting info, Figure S4).

Detecting transients at positions outside the crystal results in a completely different behaviour, c.f. Figure. 4(e) positions *C* and *D*. Here, no delayed peak is visible and the majority of photons is detected shortly after the laser pulse excitation. We conclude, that in the present case no charge carriers have passed the grain boundary and the detected signal stems solely from waveguided PL radiation, having its origin inside the initially excited crystal. If no charge carriers are transported to neighbouring crystals, the grain boundaries constitute solid walls for them. State-of-the-art synthetic routes employ an excess of lead in the precursor mixture³⁵ which leads to the formation of non-perovskite phases at the grain boundaries.^{36,37} Considering the synthesis route, which is based on the temperature-

controlled chemical conversion of a precursor film, the grain boundary can be expected to contain unconverted lead(II)-iodide precursor material. The resulting physical separation of the individual grains is expected to impede the charge transfer between grains, consistent with our PL measurements. As a side note, this process is likely to passivate the grain boundaries in a real device, which is favourable for its performance.^{38–40}

Finally, we studied the question whether the grain boundaries act as quenching sites by recording time-resolved confocal PL images. Figure 5(a) and (c) show confocal PL emission maps at two different detection time windows. In the recorded images, the grain boundaries are clearly visible as dark lines that do not emit light, which was also shown before.²⁷ In the first few nanoseconds after the excitation, a narrow region in the direct vicinity to these boundaries appears brighter than the bulk part of the crystals. At later times, this effect vanishes and within individual crystals, the emission is largely homogeneous. As noted before smaller crystals show stronger PL than larger ones.

Fig. 5(e) compares a position *A* inside a crystal corner against a position *B* in the center of the very same crystal. It is clearly visible that the transients in the center (unrestricted case) show a faster decay than near an edge.

This time-dependent PL intensity contrast seen in Figure 5 can be understood on the basis of restricted diffusion, if the grain boundaries act as solid walls for the charge carriers. When the laser excites parts in the proximity of such a wall, the generated charge carriers experience spatially restricted diffusion, because all paths through the grain boundary are forbidden. This results in a decelerated depopulation of the area, leaving more time for radiative recombination. Since in a confocal image the PL is detected from the area that was excited, within the limits of the detection point spread function, the parts near boundaries appear brighter than the bulk as long as the diffusion has not equilibrated the charge carrier concentration throughout the full crystal. If the walls would quench the PL or propel nonradiative recombination, the opposite effect would be visible and areas near the boundaries would appear dimmer than the rest. Furthermore, if there was substantial

Figure 4: Confocal PL scan (a) and detection beam PL scan (b) of the same THTO-MAPI thin film. The detection scan was recorded after excitation at the point indicated in (a). (c) Time-resolved detection beam PL images after exciting the central crystal marked in (a). Upon focused excitation the whole illuminated crystal starts to emit light after about 150 ns indicating efficient diffusive transport within the crystal. This delayed component is also seen in the transients recorded at point B. Importantly, no delayed component is observed in the transients recorded in the neighbouring crystals in the vicinity of the excitation point indicating that no charge carrier transport across crystal boundaries occurs.

charge carrier transport across the boundaries, we would not expect the edges to appear brighter. We would like to emphasize here that this distinction is difficult to make with

Figure 5: (a) Time-resolved confocal PL scan of a THTO-MAPI thin film showing the PL intensity emitted within the first 16 ns after pulsed excitation. Strikingly, regions close to crystal boundaries, corners and tips appear bright due to restricted diffusion. (b) Simulation results of the same sample area. (c), (d) Corresponding data for the time window 60 -70 ns. (e) PL transients recorded at the positions A and B indicated in (a). Sample points close to crystal edges show slower initial PL decay due to restricted carrier diffusion without indications of quenching at the boundaries.

other methods, employing large area illumination.⁴¹ The influence of restricted diffusion has been reported before for single crystalline MAPI particles by Jin et al.^{15,23} as well as for thin film microcrystals by Yang et al.²⁹ by means of microscopy, which is in agreement with our results. Both groups found no evidence for enhanced quenching or nonradiative decay at the

grain boundaries.

Another consequence of restricted diffusion near grain boundaries in the present photovoltaic material is that the charge carrier decay in smaller crystals should be slower than in larger ones and that they appear brighter in confocal PL scans. This effect was already noted in Figures. 2(b) and 4(a).

To test the hypothesis that restricted diffusion is the cause of our observations, we solved eqn. 1 numerically and included boundaries with the shape of the measured samples. We used a finite difference time domain method (see supporting information, section 4) with von Neumann boundary conditions at the grain boundaries to model solid walls. Since the excitation pulse energy in the present case was higher than for the previous measurements, mono- and bi-molecular decay channels were included in the simulation. The afore mentioned waveguiding of emitted PL was not included in the numerical simulation because the influence of grain boundaries on scattering and possible back reflections would require a nanoscopic description of the grain boundary's geometry. In order to model a confocal scan however, radiative transport is of minor importance since the main part of the PL emission stems from the excitation spot itself.

Figures 5(b) and (d) present simulation results that reproduce the main characteristics of the experimental data in (a) and (c) very well. At early times, the parts near the boundaries light up, at later times, the emission is nearly homogeneous throughout the crystal. Even small features are reproduced by the simulation. Moreover, it is possible to compare measured and simulated transients at different points of the sample. In Figure 5(e) the experimentally obtained transients at position *A* inside a corner and *B* in the center of the very same crystal are shown together with the simulated curves. Simulated and measured curves coincide nicely, only employing a global intensity scaling factor between theory and experiment and a diffusion constant of $D = 1 \text{ cm}^2/\text{s}$. As a direct consequence of restricted diffusion, the assignment of the diffusion constant by the above mentioned method using the peak position is only possible inside large crystals far away from any boundaries. The

measured curves in Figure 5(e) also emphasize that grain boundaries do not act as quenching sites, because this would result in a faster decay as compared to the crystal’s center.

In conclusion, we showed long-ranged diffusive charge carrier transport within single crystals in THTO-MAPI thin films with a diffusion constant of $D = 1 \text{ cm}^2/\text{s}$ and a longterm, monoexponential decay time of $2.5 \mu\text{s}$. At low excitation densities PL emission is longlived and within the first 200 ns does not reduce the number of charge carriers in a significant manner, which is favourable for photovoltaic devices. The time-resolved detection beam scans shows two PL components, one mediated by radiative transport and one from local charge carrier recombination. We observe that crystal boundaries act as barriers for charge carriers, only allowing for radiative transport. Because no quenching occurs at the boundaries for the present material they don’t reduce the performance in solar cell applications which exploits vertical transport in the film. Restricted charge carrier diffusion leads to a slower initial PL decay close to grain boundaries and has to be taken into account when determining the lifetime and the diffusion constant of MAPI thin films.

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Supporting Information Available

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