

Spatially resolved studies of the phases and morphology of methylammonium and formamidinium lead tri-halide perovskites

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Abstract

The family of organic-inorganic tri-halide perovskites including MA (MethylAmmonium)PbI₃, MAPbI_{3-x}Cl_x, FA (FormAmidinium)PbI₃ and FAPbBr₃ are having a tremendous impact on the field of photovoltaic cells due to the combination of their ease of deposition and high energy conversion efficiencies. Device performance, however, is known to be still significantly affected by the presence of inhomogeneities. Here we report on a study

of temperature dependent micro-photoluminescence which shows a strong spatial inhomogeneity related to the presence of microcrystalline grains, which can be both light and dark. In all of the tri-iodide based materials there is evidence that the tetragonal to orthorhombic phase transition observed around 160K does not occur uniformly across the sample with domain formation related to the underlying microcrystallite grains, some of which remain in the high temperature, tetragonal, phase even at very low temperatures. At low temperature the tetragonal domains can be significantly influenced by local defects in the layers or the introduction of residual levels of chlorine in mixed halide layers or dopant atoms such as aluminium. We see that improvements in room temperature energy conversion efficiency appear to be directly related to reductions in the proportions of the layer which remain in the tetragonal phase at low temperature. In FAPbBr_3 a more macroscopic domain structure is observed with large numbers of grains forming phase correlated regions.

Organic inorganic perovskite based solar cells have recently reached power conversion efficiencies of over 20%^{1,2}. The simple and cheap fabrication of the devices on non-crystalline substrates by vapor deposition³ or solution processing^{4,5} together with the tunability of the bandgap by chemical substitution⁶⁻⁸ has made organic inorganic perovskites very attractive materials not only for photovoltaic applications (PV), but also in light emitting diodes⁹, lasers^{10,11} and photodetectors¹². An immense effort has been made to investigate both the electronic and structural properties of these materials. This has shown that they have remarkable characteristics which make them ideally suited for device applications, such as their long diffusion lengths^{13,14}, the small binding energies of the excitons^{15,16} and radiative life times for the carriers exceeding 500 ns^{1,14,17,18}. Improving the performance of devices is leading many groups now to focus on understanding the influence of the growth conditions^{1,5,19} and passivation of the surface to suppress non radiative trap/recombination of the carriers^{18,20-22}.

However, to date relatively few studies have been performed to elucidate the influence of the microscopic structure of the perovskites on their electronic properties and crucially

the performance of devices. Only recently, confocal microscopy correlated with scanning electron microscopy (SEM) has been employed to investigate the microscopic structure of these materials¹⁷. It was shown that the emission intensity and life time of the carriers vary with position and are correlated to the presence of microcrystalline grains at a scale of a few micrometers. The weaker emission is correlated with a reduced carrier lifetime which enabled the presence of specific dark grains to be identified. In a similar microscopic study, an improvement of the life time of the carriers by employing guanidinium to reduce the number and influence of the dark grains was shown to significantly improve device performance¹⁸. Wang et al²³ have shown that doping the perovskite solution with Al^{3+} increases the structural quality of the films, leading simultaneously to improvements in the energy conversion efficiency up to 19.1% in simple MAPbI_3 films. These results show the importance of the morphology of the material, since the presence of the dark grains, acting as non radiative traps, seriously degrades the performance of devices.

A further complication in understanding the properties of the organic-inorganic tri-halide perovskites is that they show phase transitions at lower temperatures to structures with reduced symmetry. The tri-iodides transform from a tetragonal to an orthorhombic structure at around 150 K accompanied by an abrupt increase in band gap^{24–27} of ~ 100 meV. The pure tri-bromides are cubic at room temperature^{6,19}, and transform to tetragonal in the alloy family $\text{FAPbBr}_{3-x}\text{I}_x$ at around $x = 0.6$ ¹⁹. As a function of temperature the pure tri-bromides become tetragonal at around 240 K and then orthorhombic below 150 K²⁸. The transition from the cubic to the tetragonal structure appears to have no significant influence on the band gap^{15,29}, but the transition to the orthorhombic structure only produces a small increase of around 10 meV.

The temperature dependence of the band gap has previously been studied by absorption in large area samples, where the phase transition causes a continuous change of the energy of a single edge^{15,25,27}, which is most abrupt for MAPbI_3 and FAPbBr_3 while for the mixed halide alloy $\text{MAPbI}_{3-x}\text{Cl}_x$ the shift of the absorption energy is quite extended over a temper-

ature range of the order of 50 K¹⁵. In the case of MAPbI₃, it has been possible to observe the presence of two absorption edges within a few degrees of the phase transition as shown in the SI here and reported previously²⁷. This has been attributed to a coexistence of the tetragonal and orthorhombic phases for a small temperature range close to the phase transition. In MAPbI_{3-x}Cl_x, however, temperature and intensity dependent photoluminescence (PL) measurements on large area samples have been used to infer the presence of microcrystalline inclusions of the high temperature tetragonal phase at temperatures down to 4 K³⁰.

In this paper, we report on a detailed microscopic study of the family of organic-inorganic tri-halide perovskites. The chemical structure of the samples is ABX₃ where A=CH₃NH₃⁺ = MA (MethylAmmonium) or A=CH(NH₂)₂ = FA (FormAmidinium), B=Pb²⁺; and X = Cl⁻, I⁻ or Br⁻, or an alloyed combination of these. We have employed spatially resolved micro photoluminescence (μ PL) to locally probe the optical response of the films on a micrometer scale in a range of temperatures from 4 K up to 300 K. All the samples studied show the presence of both dark and bright grains, independently of the temperature. Additionally, in all of the compounds investigated there is evidence that the tetrahedral to orthorhombic phase transition observed around 160 K does not occur uniformly across the sample. Domains of the high temperature phase remain even at very low temperatures and the relative importance and behavior of these can be significantly altered by the presence of local perturbations to the layer morphology. The processes which reduce the proportion of domains at low temperatures appear to be strongly correlated with improvements in the room temperature energy conversion efficiency. A particularly dramatic example of this is seen with the introduction of Al doping, where despite there being little change in domain size the devices show significantly higher conversion efficiencies when the phase transition to the orthorhombic phase is more uniform, and less of the tetragonal phase remains at low temperature.

The μ PL reveals that the emission behaviour is strongly dependent on both temperature and position. At high temperatures (>200 K), the spectra show only a single emission

peak at an energy ~ 20 meV below the band gap deduced from absorption as shown in Fig 1, suggesting that emission is dominated by an essentially free exciton state. The room temperature integrated emission maps are shown in Fig. 2 (a) - (c) for MAPbI₃, MAPbI_{3-x}Cl_x and FAPbBr₃ respectively, where the intensity varies across the scanned area showing brighter and darker emission areas. This is similar to previous observations of dark and bright grains for MAPbI₃¹⁷. All three compounds show similar behaviour, consistent with the microcrystalline grain structure known to be present in such thin layer perovskites, however it is noticeable that the microcrystallites for the mixed halide MAPbI_{3-x}Cl_x are significantly larger, consistent with their usually better device performance and photoluminescence emission^{12,14}.

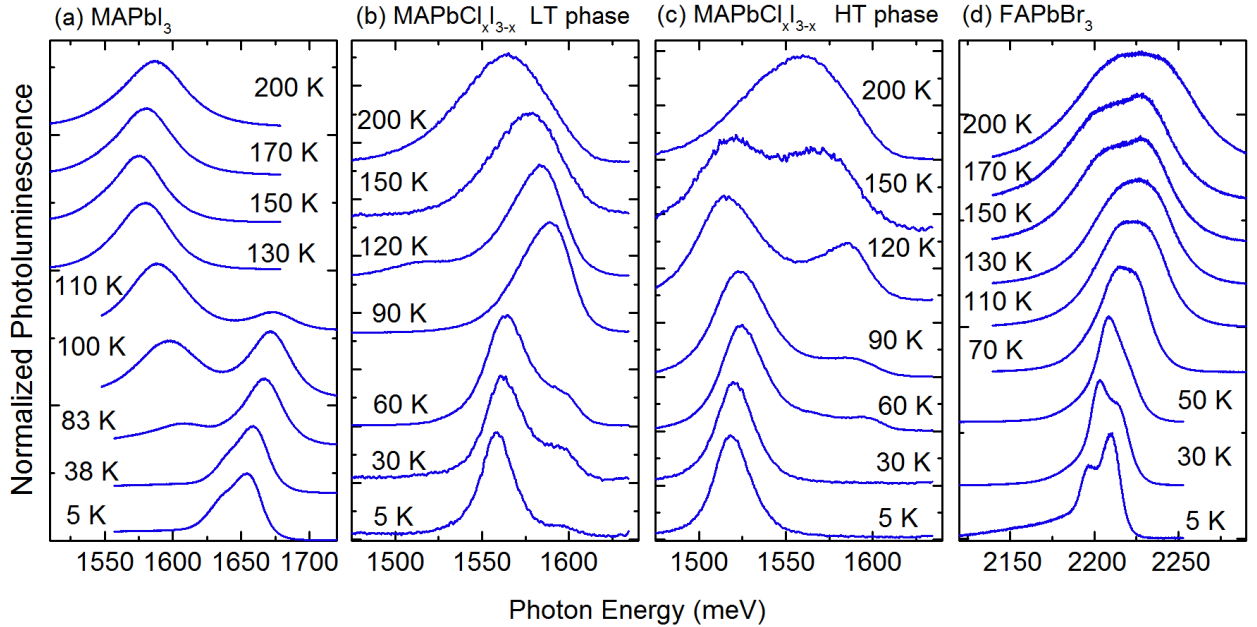


Figure 1: Temperature dependence of the μ PL spectra for (a) MAPbI₃, (b) and (c) two different spot positions on MAPbI_{3-x}Cl_x corresponding to domains of the orthorhombic and tetragonal phases and (d) FAPbBr₃.

At lower temperatures there are significant changes in behaviour as the spectral emission develops considerable positional dependence below the tetragonal to orthorhombic phase transition temperature of 155 K. Fig. 1(a) shows spectra at a typical location for MAPbI₃ as a function of temperature. Around and below the temperature where the phase transi-

tion occurs we observe a second peak at higher energy (1665 meV), corresponding to the orthorhombic phase (OP)^{25,31,32}. It is noticeable, however, that the emission peak at lower energy (~ 1590 meV) remains dominant down to much lower temperatures than those where the edge can be seen in absorption (as shown in S.I. Fig. 1 (a)) and only disappears at temperatures below ~ 80 K. The main peak also has a small shoulder on the low energy side at ~ 1635 meV, which suggests that emission from bound excitons, or possibly donor-acceptor-pair transitions³², may also be occurring in the majority, orthorhombic, phase. Emission from the low energy peak, which we infer is due to microcrystallite domains of the high temperature tetragonal phase (TP), is however found to have a strong spatial dependence. Low temperature (4 K) mapping results for MAPbI₃ are presented in Fig. 3 where the intensity of the blue colour in panel (a) indicates the integrated intensity of the dominant OP peak. The emission is relatively uniform while still showing some variation on the scale of a few μm due to the underlying microcrystalline structure, as seen at high temperature. In addition, however, the low energy, TP, peak at ~ 1585 meV can still be detected at certain positions within the sample. Typical spectra for two different points on the sample are shown in panel (c), where in one location we observe peaks from both phases and in the other only one is visible. The emission energy of the TP peak, approximately 80 meV lower in energy, is shifted down by the same amount as the change in band gap observed at the phase transition temperature as shown in Fig. 1(b) of the SI. The intensity of the TP peak is always weaker than the intensity of the OP peak, however the presence of the TP peak does appear to cause some decrease in the intensity of the OP peak. In panel (b), we show the integrated intensity of the TP peak in red superimposed upon the integrated intensity of the OP peak. This shows a rather sparse distribution of isolated regions where the TP peak is present with a typical size of order 1-5 μm , usually where the intensity of the OP peak is weaker. To test for correlation between the two peaks, in panel (d) we plot the proportion of the total emission in each peak ($\frac{I_{OP,TP}}{(I_{OP}+I_{TP})}$) as a function of the emission intensity of the TP peak (I_{TP}). As the proportion of the emission in the TP peak (orange points) rises, the OP phase

falls progressively.

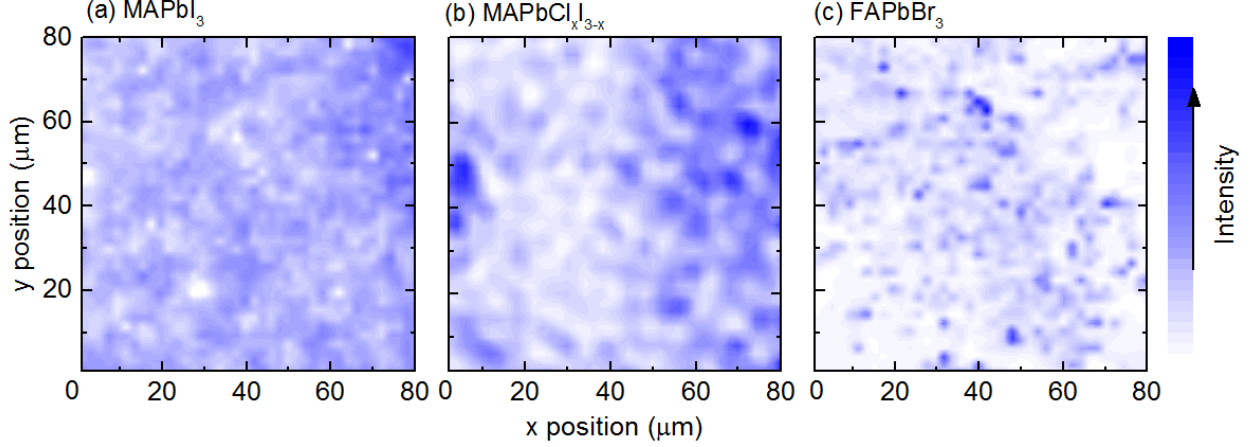


Figure 2: Integrated intensity of the μ PL peak as a function of the position for (a) MAPbI_3 , spot illumination intensity 40 nW, (b) $\text{MAPbI}_{3-x}\text{Cl}_x$, spot illumination intensity 60 nW, and (c) FAPbBr_3 , spot illumination intensity 100 nW, respectively at 300K. The scanning step is $2\mu\text{m}$.

Overall this behaviour provides strong evidence for the coexistence of the two crystal phases at low temperature, with the existence of a small number of microdomains of the high temperature tetragonal phase which are capable of preferentially collecting free carriers due to their smaller band gap as suggested previously for $\text{MAPbI}_{3-x}\text{Cl}_x$ ³⁰. Further evidence to support this assignment has recently been reported⁷ which shows that hysteresis in the emission maps can be strongly correlated with hysteresis observed in X-ray analysis of the films. This is consistent with the observation of a dominant TP peak in PL at temperatures significantly below the phase transition, whereas it cannot be observed directly in absorption. Typical separations of the tetragonal inclusions are of the order of $10 - 20\mu\text{m}$, suggesting that the diffusion length in this material remains at around this value until the temperature falls below 80 K and that inter grain diffusion is significant in this temperature regime. Since the μ PL is obtained by scanning the exciting laser and the diffusion length will be $\propto \sqrt{T}$ at low temperatures, the low temperature maps provide an upper limit to the size of high temperature phase domains of a few μm , which is comparable with the size of individual crystallites. In practice, they may be even smaller than this since the relatively long diffusion

lengths observed in perovskites^{13,14} mean that even microscopically small regions of smaller band gap material can be expected to collect excitons over distances comparable to the diffusion length. As a consequence these small regions can dominate the PL response without being detectable in absorption measurements. We estimate the proportion of the layer which shows some detectable emission feature from the high temperature tetragonal phase ($I_{TP} > 5\%I_{OP}$) to be on the order of 20% of the total area, as shown in Table 1. Such co-existing crystal phases have been observed previously in a number of different perovskite materials, often associated with the presence of strain^{33,34}.

In addition, we have performed the same measurements and analysis on a thin film of MAPbI₃, doped with Al during an otherwise identical film preparation. This is important from an applications point of view since it has recently been shown that doping with Al dramatically improves the quality of the film resulting in conversion efficiencies of up to 19.1%²³ at an optimum doping level of 0.15mol%. The results are presented in Fig 3(e)-(h). In contrast to the pure MAPbI₃ film, the doped material shows very few of the tetragonal inclusions at low temperature. This is clearly seen in Fig 3(f) where the intensities of the crystal phases are superimposed and is further evident in the correlation plotted in panel (h). The area of the film which shows emission from the tetragonal phase is greatly reduced and more than $\simeq 99\%$ of the film only shows emission related to the pure orthorhombic phase. We propose that there is a direct correlation between the good room temperature device performance and the low temperature microscopic phase uniformity.

The presence of high temperature, tetragonal phase, domains becomes more obvious in the larger grains which are known to form^{12,35} in MAPbI_{3-x}Cl_x as shown in Fig. 4 where the spatial mapping measured at 4 K and 150 K is shown. In both cases the spectra show at least two well resolved emission peaks at different spatial positions as shown in panels (c) and (g). Panels (a) and (e) show maps at 4 K and 150 K respectively, based on the intensity of the OP peak, which as above corresponds to the low temperature crystal phase. We observe the same the grain structure as at room temperature with typical grain sizes in the region of 5-10

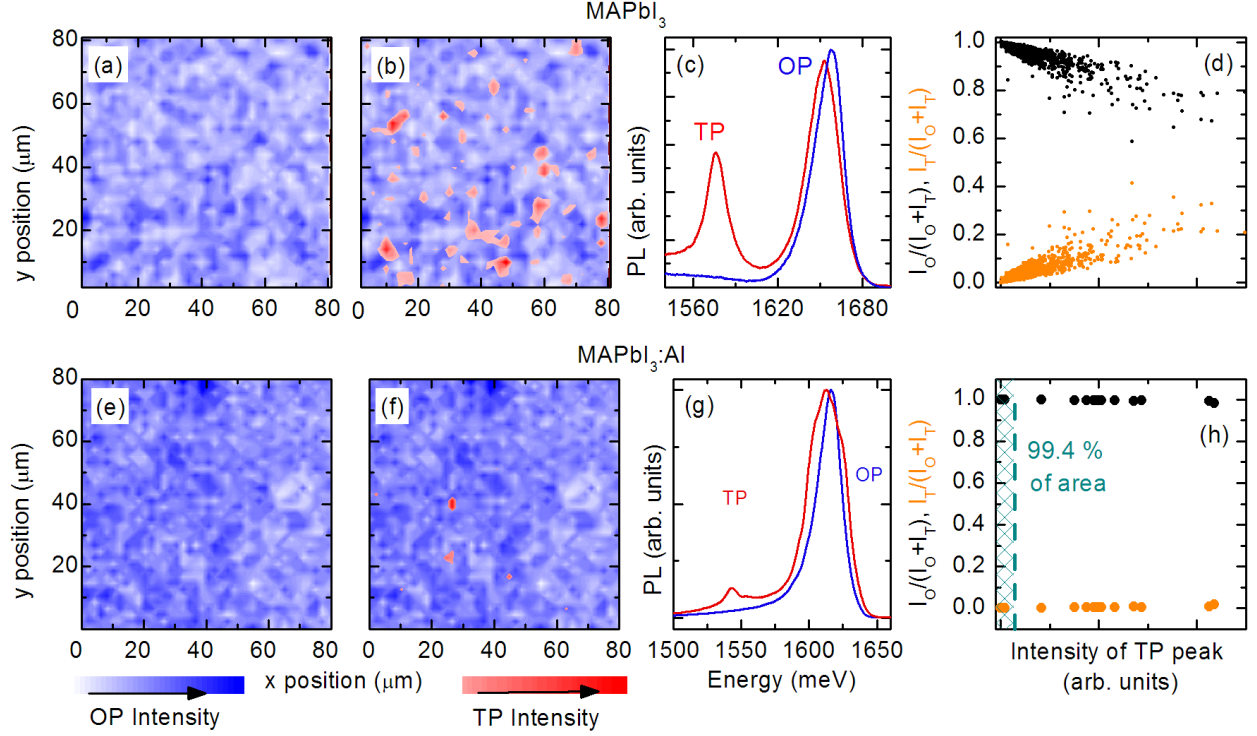


Figure 3: (a) Integrated intensity of the high energy (OP) peak as a function of position. The intensity increases from white to dark blue. The scanning step is $2\mu\text{m}$. (b) A second map of the low energy (TP) peak is superimposed onto the map shown in (a). The intensity increases from white to red. (c) Typical spectra for positions where only the OP peak was observed (blue) and where both peaks were observed (red). (d) Correlation of the integrated intensity of the TP (orange) and OP (black) peaks versus intensity of the low energy TP peak. (e) - (h) show the same measurements performed on the film doped with 0.15mol% Al. All the measurements have been performed at 4K, spot illumination intensity 5 nW.

μm . However, when we superimpose an additional intensity map for the TP peak as shown in the panels (b) and (f) for 4 K and 150 K respectively, we observe that the areas with weak emission from the low temperature phase correspond very clearly with strong emission from the TP peaks. This is particularly obvious at 4 K, where almost the whole sample becomes uniformly emissive from either one peak or the other. This suggests a strong anti correlation between the two sets of domains which we associate with individual crystallites being in either one crystal phase or the other. The anti correlation is confirmed by plotting $(\frac{I_{OP,TP}}{I_{OP}+I_{TP}})$ as before in Fig. 4(d) and (h) for 4 K and 150 K respectively. In both cases there is a clear anti correlation, when the intensity of the TP peak reaches its maximum, the intensity of the

OP peak is minimal. The larger scale of the crystallite domains also allows the two different phases to be completely resolved. Fig. 1(b) and (c) show the completely different temperature dependence of the emission spectra for two microdomains which in Fig. 1(b) transforms from the tetragonal to the orthorhombic phase at low temperature, while the region in Fig. 1(c) remains in the tetragonal phase for the whole temperature range. In Fig. 1(b), all sign of the TP peak disappears below 120 K and the low temperature, orthorhombic phase initially shows a higher energy peak at around 1600 meV which we attribute to the free exciton, which is replaced below 60 K by a lower energy peak at ~ 1560 meV, presumed to be some form of bound exciton state. By contrast Fig. 1(c) shows spectra where the strongest feature is always the TP peak which becomes progressively more dominant as the temperature falls. By 30 K only a single peak can be seen at ~ 1525 meV which is again shifted down by the energy difference between the orthorhombic and tetragonal phases at the high temperature and no trace of the OP peak can be detected. The fraction of the film area showing emission from the TP at low temperature is significantly lower than for the MAPbI₃, but both the scale of the domains and their separation has increased by a factor consistent with the increased size of the microcrystallites.

Overall the three MAPbI₃-like samples show a consistent correlation between the proportion of the films showing uniform OP emission at low temperatures and the room temperature energy conversion efficiencies as shown in Table 1. The presence of Cl in the film growth is known to produce enhanced device performance^{4,12} despite it being difficult to detect in substantial quantities in the final layers³⁵, while only very small levels of Al doping can produce significant device performance enhancement²³. Both Cl and Al have had a similarly strong influence on the uniformity of the structural phase transition which suggests that the device performance improvements are strongly linked to the changed crystallinity within the individual grains which enhances the uniformity of the phase transition and inhibits the persistence of the TP domains at low temperature. The improved crystallinity has been demonstrated by Wang et al²³ who have shown, from X-ray diffraction linewidths,

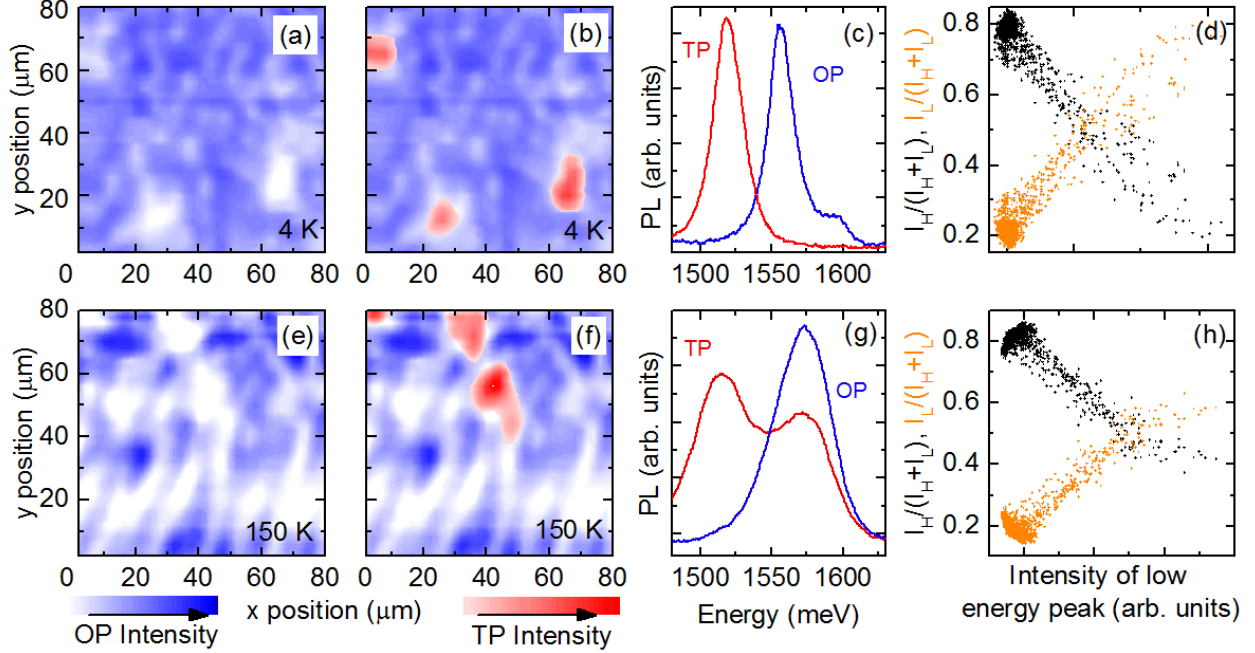


Figure 4: (a) Integrated intensity of the high energy (OP) peak as a function of position. The intensity increases from white to dark blue. (b) A second map of the low energy (TP) peak is superimposed onto the map shown in (a). The intensity increases from white to red. (c) Typical spectra for positions where only the OP peak was observed (blue) and where the TP peak was seen also (red). (d) Correlation of the integrated intensity of the TP (orange) and OP (black) peaks versus intensity of the low energy TP peak. (a)-(d) were performed at 4K, spot illumination intensity 0.3 nW, and (e)-(h) show the same measurements performed at 150K, spot illumination intensity 3 nW. The scanning step was $2\mu\text{m}$.

that non-uniform microstrain which is related to crystal imperfections such as dislocations, vacancies, stacking faults, interstitials, twinning and grain boundaries^{36,37}, is minimized at the optimum doping level. It is remarkable that the low temperature properties of the films should be so clearly linked to the high temperature device performance.

In addition to the apparently random presence of the TP domains shown in Figures 3 and 4, there is also evidence that the presence of the different phases can be significantly influenced by local perturbations to the layer morphology. This is shown in Fig. 2 and Fig. 3 of the S.I. for $\text{MAPbI}_{3-x}\text{Cl}_x$ where the low temperature image Fig. 2 (S.I.) shows a very clear physical pattern, associated probably with a crack or fissure of over $100\mu\text{m}$ in length. This is visible as a positive image for the tetragonal phase emission at 1535 meV and as an equivalent negative image from the intensity map for the free and bound exciton peaks at 1565 and

Table 1: Champion energy conversion efficiencies (PCE) measured for cells fabricated using the same or comparable iodine-based Methylammonium compounds compared with the amount of tetragonal phase inclusions within the film at low temperature.*****A similar difference (16.2% versus 18.3%) was observed comparing a batch average PCE of 20 devices made from the undoped and Al doped MAPbI₃ samples**²³

Compound	MAPbI ₃	MAPbI _{3-x} Cl _x	MAPbI ₃ :Al
Champion PCE (%)	17.1 ²³	17.3 ³⁸ -18.4 ³⁹	19.1 ²³
% of TP inclusions	20.6	9.8	0.6
microstrain lattice broadening ^{23,37}	0.65%	N/A	0.52%

1600 meV from the dominant orthorhombic low temperature phase. Fig. 3 (S.I.) shows a further low temperature image, where a small region of material has been photo-annealed with a focussed spot of 532 nm radiation creating local damage or phase modification. At the centre of the annealing there is a dark core around which the emission becomes dominated by a domain of the tetragonal high temperature phase, followed sequentially by emission rings from the OP bound exciton, the OP free exciton and finally back to a macroscopically uniform region dominated by the OP bound exciton again, as shown previously in Fig 1. It has been observed^{40,41} that photo-annealing causes iodine diffusion leading to a reduction in iodine density in the centre of a focussed spot surrounded by an increase in iodine content. This would suggest that the local high temperature phase inclusions are strongly associated with a reduced iodine content, possibly associated with an enhanced level of iodine vacancies which are known to influence charge trapping and nonradiative recombination⁴² and that the iodine content is also responsible for influencing strongly the relative emission strength from bound and free excitons in the low temperature phase. This would also be consistent with the idea that the iodine content could be significantly perturbed close to the edges of cracks formed during film deposition.

We have also repeated the μ PL studies for FAPbI₃. This shows a comparable behaviour at low temperatures (S.I. Fig. 4(a)) to that seen for MAPbI₃ with a few small microcrystallite grains on a scale of 1-5 μ m, which remain within the high temperature, tetragonal, phase giving a TP peak emission, and occupying at most a few percent of the total sample area.

It also demonstrates a similar role played by the presence of “cracks” as can be seen in Fig. SI 4(b) at 4 K. There is a large dark crack or scar running through the centre of the image which is bordered by a region of tetragonal material, again suggestive of an enhanced concentration of iodine vacancies. Beyond this the material returns to the same distribution of a few microcrystallite grains of high temperature phase in the main body of the sample.

We now turn to the case of FAPbBr_3 , which shows significantly different behaviour to that seen for the iodides and the $\text{MAI}_{3-x}\text{Cl}_x$ alloy. The temperature dependence of the emission spectra for one region of the sample is shown in Fig. 1(d). In this case there is no clear separation of two peaks which can be easily associated with the different phases but the spectra do show the disappearance of a low energy component at around the *****tetragonal to orthorhombic** phase transition temperature of 150 - 160 K, leaving two strong peaks at around 2190 and 2205 meV at low temperature. *****By room temperature the material becomes cubic⁷, but shows no significant further change in the PL emission spectrum and the** room temperature μPL mapping, as shown in Fig. 2, demonstrates that there is a similar grain structure and size to that seen for the MAPbI_3 and FAPbI_3 . The low temperature mapping shown in Fig. 5 demonstrates, however, completely different behaviour. In this case we see variations in the emission spectra on a much larger physical scale as compared to that seen for the iodide samples. This suggests that the phase domain structure for the bromide is independent of the grain structure of the layer. Fig. 5(a) shows that when imaged at 2205 meV, large areas of the film do not emit. Imaging at 2190 meV, however, we see in Fig. 5(b) that there is a complementary emission, as marked in red, which corresponds very well with the non emitting area of the low temperature orthogonal phase and Fig. 5(c) shows that the spectra from the two different regions are well resolved. This suggests that macroscopic domains exist consisting of multiple microcrystallites, which can be either orthorhombic or tetragonal at low temperatures with typical domain sizes on the order of 100 μm or more. The difference in the emission energies of only 15 meV between the two regions suggests that there is very little difference in band structure or free

energy between the two phases as has been shown previously²⁹, which would allow the phase transition to propagate more easily thus creating macroscopic domains.

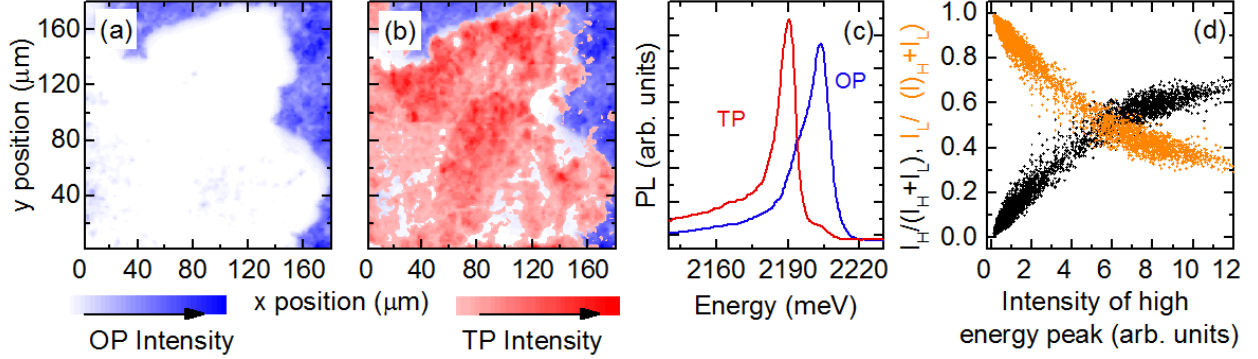


Figure 5: (a) Integrated intensity of the high energy (OP) peak as a function of position. The intensity increases from white to dark blue. The scanning step was $2\mu\text{m}$. (b) A second map of the low energy (TP) peak is superimposed onto the map shown in (a). The intensity increases from white to red. (c) Typical spectra for positions where only the OP peak was observed (blue) and where both peaks were observed (red). (d) Correlation of the integrated intensity of the TP (orange) and OP (black) peaks versus intensity of the TP peak. All the measurements were performed at 4K, spot illumination intensity 5 nW.

In conclusion we have demonstrated the existence of a microscopic mixed phase domain structure in the tri-iodide organic-inorganic perovskites at temperatures well below the tetragonal to orthorhombic phase transition. The scale of the domains is strongly related to the underlying microcrystalline structure and corresponds to individual crystallites which adopt one or the other crystal structure, such that a significant percentage of the final layer can remain within the high temperature tetragonal phase, even at 4 K. Remarkably, growth methods which reduce the proportion of the tetragonal phase domains at low temperature are clearly correlated with improved room temperature PV device performance. The existence of even a small proportion of material in these domains could easily allow them to dominate the emission properties, particularly at higher temperatures, where the diffusion lengths can be very long^{13,14} and we expect that their presence is likely to be very significant for the performance of optoelectronic devices such as both PV devices and perovskite based lasers¹¹. By contrast the tri-bromide FAPbBr_3 shows a much more macroscopic phase domain structure which is independent of the crystallites, probably associated with the very

small energetic difference between the two crystal structures, which suggests that the tri-Bromides might be significantly better in device applications. We have also demonstrated that the presence of strains or local damage can have a significant effect on the domain structure, producing localised regions of phase modification, which also suggests that elimination of such features should be an important goal for device optimisation.

Experimental Method

Perovskite precursor synthesis: Formamidinium iodide (FAI) and formamidinium bromide (FABr) were synthesised by dissolving formamidinium acetate powder in a 1.5x molar excess of 57% w/w hydroiodic acid (for FAI) or 48% w/w hydrobromic acid (for FABr). After addition of acid the solution was left stirring for 10 minutes at 50° C. Upon drying at 100°C, a yellow-white powder is formed. This was then washed twice with diethyl ether and recrystallized with ethanol, to form white needle-like crystals. Before use, it was dried overnight in a vacuum oven. To form FAPbI₃ and FAPbBr₃ precursor solutions, FAI and PbI₂ or FABr and PbBr₂ were dissolved in anhydrous N,N-dimethylformamide (DMF) in a 1:1 molar ratio, at 0.55M of each reagent, to give a 0.55M perovskite precursor solution. To form CH₃NH₃PbI_{3-x}Cl_x precursor solutions, Methylammonium iodide (MAI) and lead chloride (PbCl₂) were dissolved in a 40% w/w DMF solution in a 3:1 molar ratio. For MAPbI₃, precursor solutions were prepared from a precursor solution, prepared by mixing methylammonium iodide (Dyesol) and lead acetate trihydrate (Aldrich) at a 3:1 molar ratio, then dissolved in anhydrous N,N-Dimethylformamide with final concentrations of 30 wt% with the addition of hypophosphorous acid (3 μ l/ml) as previously reported by Zhang et al.⁴³. For Al³⁺-doped CH₃NH₃PbI₃, Aluminium acetylacetonate (Al-acac₃) was added into the MAPbI₃ precursor solution at the desired Al³⁺/Pb²⁺ ratio of 0.15 mol%. (i.e. we add 0.3 mg of Al-acac₃ into 1 g MAPbI₃ precursor solution to achieve 0.15 mol% Al-acac₃ doping.).

Film formation: All the samples were prepared in a nitrogen-filled glovebox on glass sub-

strates cleaned sequentially in hallmanex, acetone, isopropanol and O_2 plasma. Immediately prior to the Formamidinium (FA) sample film formation, small amounts of acid were added to the precursor solutions to enhance the solubility of the precursors and allow smooth and uniform film formation. $38\mu\text{l}$ of hydroiodic acid (57% w/w) was added to 1ml of the 0.55M FAPbI_3 precursor solution, and $32\mu\text{l}$ of hydrobromic acid (48% w/w) was added to 1ml of the 0.55M FAPbBr_3 precursor solution. FA Films were then spin-coated from the precursor plus acid solution on warm (85°C) substrates for 45s at 2000rpm, followed by annealing at 170°C in air for 10 minutes. This gave very uniform pinhole-free layers, 350nm thick, of FAPbI_3 or FAPbBr_3 .

The Methylammonium (MA) samples were prepared following methods described previously^{4,35,39}. In brief, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films were prepared by spin-coating for 60s at 2000 rpm on warm (85°C) substrates, followed by annealing at 100°C in air for 1 hour. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were prepared by spin-coating at 2000 rpm for 45s from the as-prepared precursor solution, drying 10 min on the bench in the glovebox, followed by annealing at 100°C for 5 min.

Reproducibility: Sample films of $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, FAPbI_3 and FAPbBr_3 were all deposited and measured on at least 2 independent runs each, which demonstrated that the data showed a high degree of batch and measurement consistency as shown in Figs 5 and 6 of the S.I.

All films were all sealed by spin-coating a layer of the insulating polymer poly(methyl methacrylate) (PMMA) at 1000 rpm for 60s (precursor solution 10mg/ml in chlorobenzene) on top in order to ensure air-and moisture-insensitivity.

For the optical measurements the sample was placed in a helium flow cryostat with optical access with the accessible temperature range 3 – 300 K. Excitation and collection was implemented using a microscope objective with a numerical aperture $\text{NA} = 0.55$ and magnification $50\times$. The typical diameter of the spot was of the order of $1\mu\text{m}$. Additionally, the cryostat was mounted on motorized $x - y$ translation stages to allow high resolution

spatial mapping. The μ PL spectra have been recorded using a spectrometer equipped with a CCD camera. A green solid-state laser, emitting at 532 nm, was used for excitation.

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Supplementary Information: Spatially resolved studies of the phases and morphology of methylammonium and formamidinium lead tri-halide perovskites

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Fig. 1 of the supplementary information presents macro-transmission (transmission of white light averaged over 1 mm² spot) measured as a function of the temperature for MAPbI₃. Panel (a) contains the transmission spectra taken at different temperatures, and panel (b) shows resulting absorption energies plotted as a function of the temperature. At temperatures around the phase transition (150-170 K) the spectra reveal presence of both

orthorhombic (orthorhombic phase, OP) and tetragonal (tetragonal phase, TP) phases. The phase transition from tetragonal to orthorhombic phase causes an abrupt rise of around 100 meV in the energy of the absorption edge. The temperature dependence of the TP peak reveals a turning point at 168 K (b). No trace of the OP is found above 170 K in transmission and in both temperature dependent and spatially resolved μ -PL studies, suggesting that above 168 K the material is entirely in the tetragonal phase.

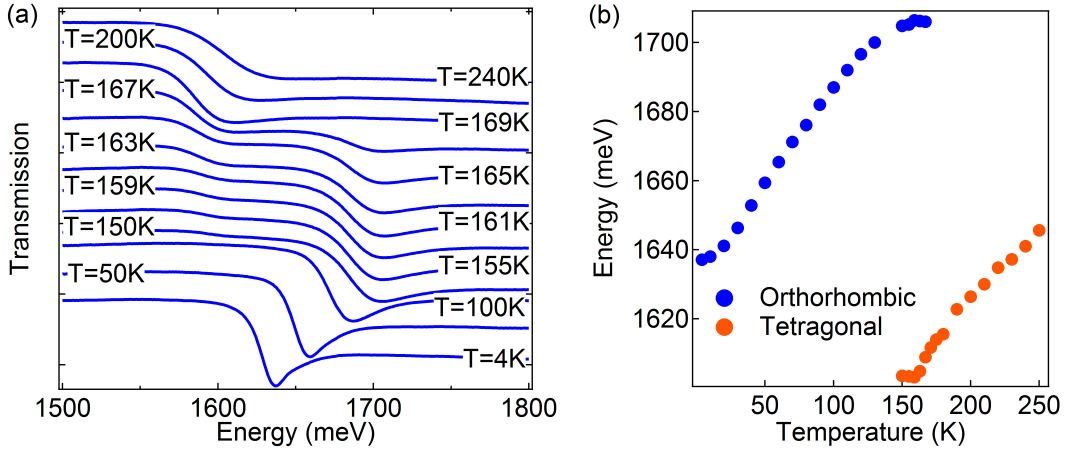


Figure 1: **Temperature dependence for MAPbI₃ in macro transmission.** (a) Transmission spectra and (b) energy of the absorption edge as a function of temperature.

Fig. 2 shows a low-temperature (5 K) μ -PL map of a selected region of a MAPbCl_xI_{3-x} sample. This demonstrates an obvious positive/negative correlation between the peaks at 1535 meV and 1565/1600 meV. As stated in the main article, we attribute the 1535 meV emission (panel a) to high temperature, tetragonal phase and the 1565 (panel b)/1600 meV (panel c) peaks respectively to bound and free exciton of the low temperature, orthorhombic phase. The positive/negative correlation of the OP and TP peaks is particularly clear for the narrow-strip regions with well-defined borders (compare panels (a) and (b)). This may suggest an enhanced presence of the of high temperature phase in strained or cracked areas. There is also significantly more variation in the intensity of the bound exciton when compared to the free exciton for the OP phase, which is found to be most strongly quenched in the regions close to the tetragonal phase inclusions (c).

Further conclusions about the nature of observed inhomogenities come from an investi-

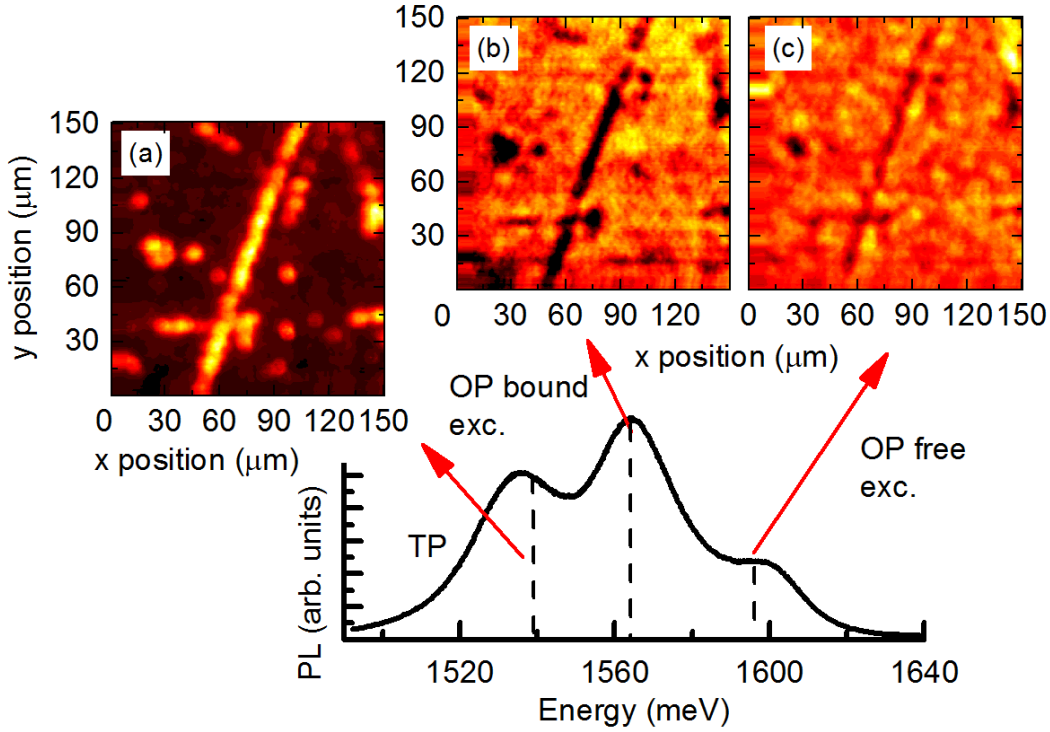


Figure 2: **Spatially resolved micro-photoluminescence for $\text{MAPbI}_{3-x}\text{Cl}_x$ at $T = 5$ K, scanning step $1 \mu\text{m}$.** Photoluminescence spectrum and integrated intensity maps of the sample corresponding to: (a) high temperature, TP peak and bound (b) and free (c) exciton peaks of the low temperature OP.

gation of regions exposed to a focused laser spot. It has been reported recently¹, that photo-annealing induces the migration of halide ions away from the point of exposure, influencing the PL properties of the material. Fig. 3 presents low temperature spatially resolved micro-photoluminescence for a $\text{MAPbCl}_x\text{I}_{3-x}$ sample illuminated for several minutes with a 532 nm laser spot of 10^9 W/m^2 power density at room temperature. As a result of photo annealing, regions of decreased and enhanced halide content are formed Fig. 3 (a), leading to emissions characteristic of both the tetragonal phase and both excitons of the orthorhombic phase (e). The center of the laser spot is a dark core (upper right corner of the maps). Moving away from the dark core (with a probably increasing iodine content), we find regions of TP emission (b). Sequentially, we observe rings of emission from OP bound excitons, OP free excitons (d) and then again OP bound excitons which are dominant in the unaffected areas.

This picture is consistent with the emission being controlled by an iodine content as shown in panel (a), where OP free excitons are only dominant at low temperatures in regions of enhanced iodine content.

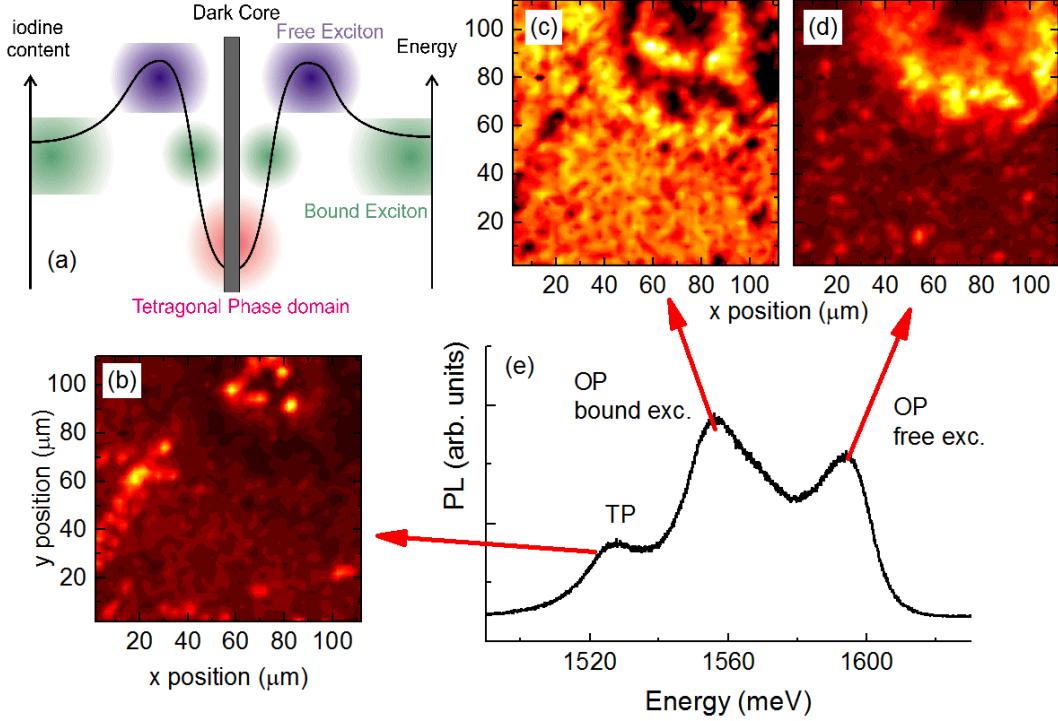


Figure 3: **Spatially resolved micro-photoluminescence for $\text{MAPbI}_{3-x}\text{Cl}_x$ at $T = 10$ K, scanning step $2 \mu\text{m}$** (a) the distribution of iodine ions as a function of distance from the point of exposure. (b)-(d) integrated intensity maps of the sample corresponding to: (b) high temperature, TP peak and bound (c) and free (d) exciton peaks of the low temperature OP. (e) Photoluminescence spectrum showing all observed transitions.

We supplement the spatially resolved μ -PL obtained for MAPbI_3 with measurements performed on compounds based on the Formamidinium cation, FAPbI_3 (Fig.4). We show a predominantly uniform region (panels a- d) and an area in proximity of a dark ribbon, being probably a crack or fissure (panels d-h). Similarly to MAPbI_3 , at low temperatures we observe the anti correlation of the OP and TP emission peaks, with TP phase grains up to $10 \mu\text{m}$ in size (panels a and b). Both bound and free excitons of OP occur simultaneously in the investigated region (c). The regions close to the dark ribbon (panels (d)-(e)) show a 1D analogy of the photo-annealing results. Close to the ribbon, we observe enhanced emission

from the TP peak, with additional narrow emission lines probably from localized states (g). In addition the TP/OP anticorrelation is significantly stronger than in the case of the region shown in (a) (compare panels d and h). This gives further evidence to link the existence of the tetragonal phase inclusions with the presence of strained or defected areas.

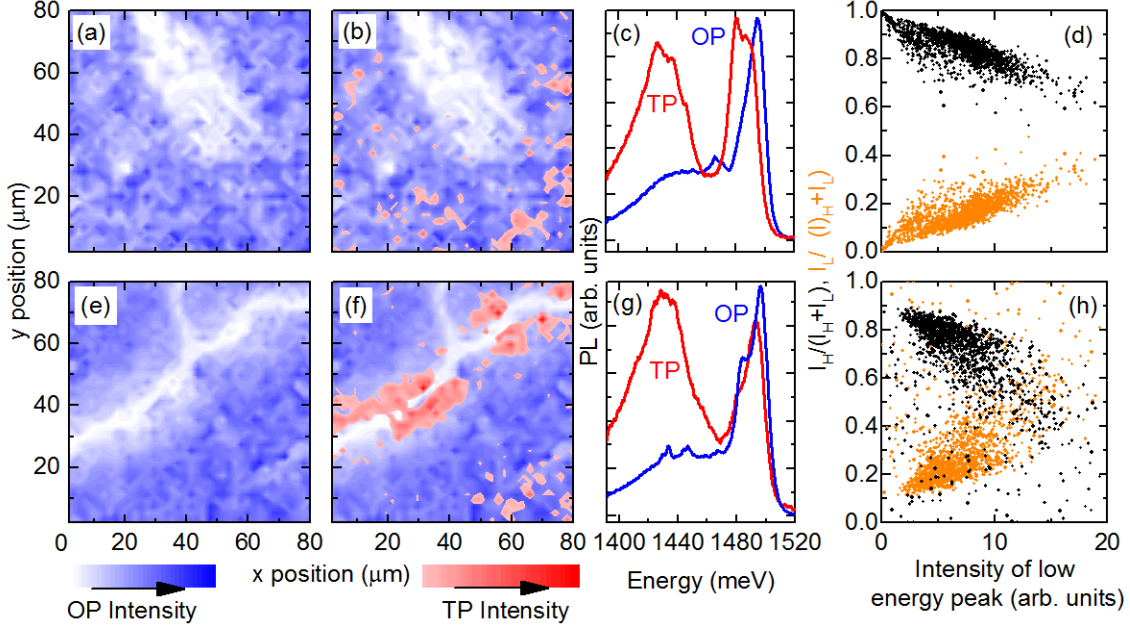


Figure 4: **Spatially resolved micro-photoluminescence for FAPbI₃ at $T = 5$ K, scanning step $2\mu\text{m}$.** The images present a homogenous area (a)-(d) and a region around dark ribbon (e)-(h). (a),(e): Integrated intensity of the OP peak across the sample. The intensity increases from white to dark blue. (b),(f): Two maps of the integrated intensity of the OP and TP peaks. The intensity of the OP (TP) is marked in blue (red) respectively. (c),(g): Typical photoluminescence spectra with dominance of OP (blue) and TP (red) peaks. (d),(h): Correlation of the integrated intensity of the TP (orange) and OP (black) peaks versus intensity of the TP peak.

In order to demonstrate the batch to batch and measurement to measurement reproducibility we compare examples of the same batch mapped with two different mapping systems in different laboratories Fig.5 and of two separate batches made approximately one year apart mapped with the same system Fig.6.

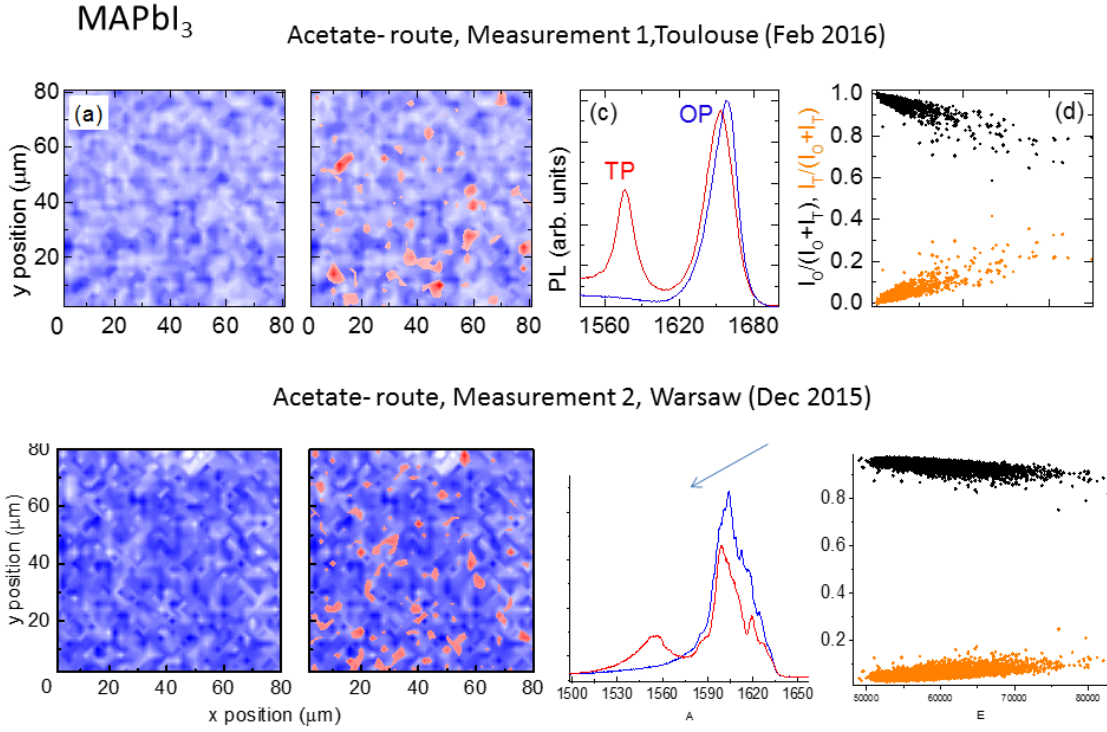


Figure 5: **Spatially resolved micro-photoluminescence for MAPbI₃ at $T = 5$ K, scanning step $2\mu\text{m}$.** The two sets of images and spectra were taken using similar mapping systems located in Toulouse and Warsaw, approximately 3 months apart, using samples fabricated at the same time.

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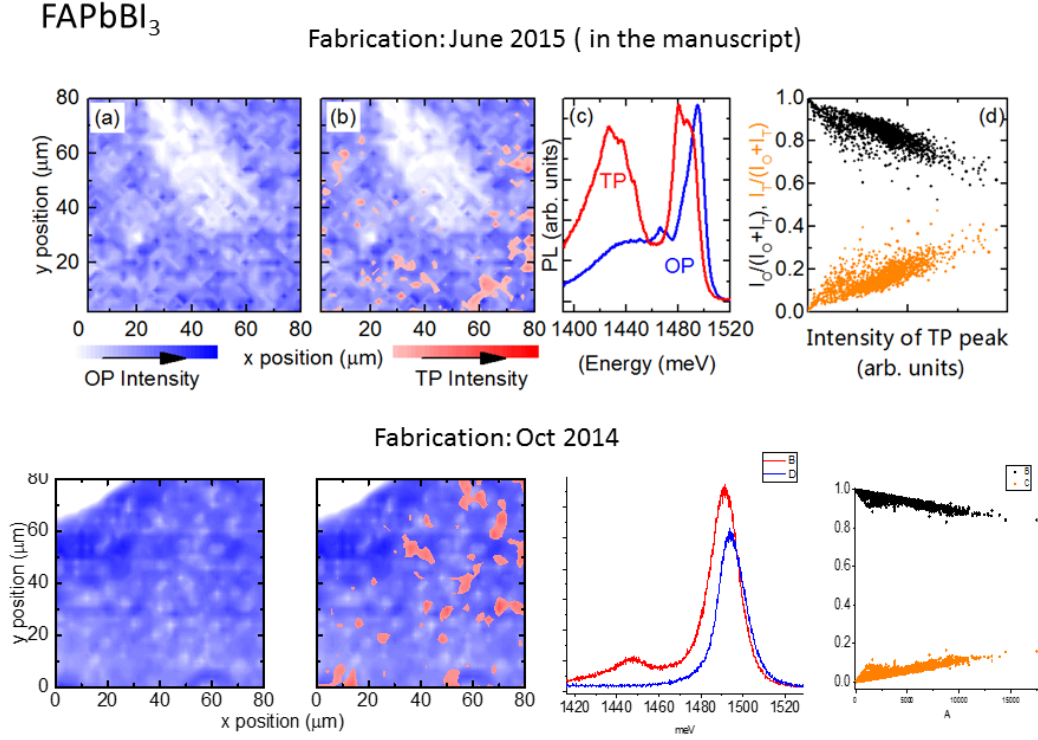


Figure 6: **Spatially resolved micro-photoluminescence for FAPbI₃ at $T = 5$ K, scanning step $2\mu\text{m}$.** The two sets of images and spectra were taken from samples fabricated approximately one year apart.