Local Rearrangement of Iodide Defect Structure Determines Phase Segregation Effect in Mixed Halide Perovskites

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ABSTRACT

Mixed-halide perovskites represent a particularly relevant case within the family of lead-halide perovskites. Beyond their technological relevance for a variety of optoelectronic devices, photo-induced structural changes characteristic of this type of materials lead to extreme photophysical changes that are currently the subject of an intense debate. Herein we show that the conspicuous photoinduced phase segregation characteristic of these materials is primarily the result of the local and metastable rearrangement of the iodide sublattice. A local photophysical study comprising spectrally-resolved laser scanning confocal microscopy is employed to find a correlation between defect density and the dynamics of photo-induced changes, which extend far from the illuminated region. We observe that iodide rich regions evolve much faster from highly defective regions. Also, by altering the material composition, we find evidence for the interplay between iodide-related defect distribution and the intra and inter domain migration dynamics giving rise to the complexity of this process.

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With efficiency reports in solar cells¹ and light emitting devices (LEDs)² pairing or outperforming any other solution process technology achieved over less than a decade, lead halide perovskites (LHP) have emerged as one of the most technologically relevant materials of the 21st century. However one of the main bottlenecks for their commercialization is their instability against external stimuli and in particular against illumination. In this respect a material that epitomizes such instability are mixed-halide perovskites (mLHP) with general formula $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_x\text{Br}_{1-x})_3$ whose electronic bandgap can be tuned across the visible³ by using a combination of halides in the appropriate ratio to form solid alloys that can be incorporated into tandem solar cells,⁴ LEDs⁵ or lasers.⁶ Upon illumination mLHP undergo structural changes leading to the formation of I-rich regions with composition $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ ⁷ (a further compositional change being prevented by the presence of a phase transition³) towards which photo generated carriers are funneled, negatively affecting the performance of photovoltaic devices and LEDs.^{8,9,10}

While the ultimate mechanism behind the formation of I-rich domains is still under debate, some factors have been identified to play a key role. The observed spectral changes involve a redistribution of the halide component through ionic migration and therefore the presence of halide-related defects is necessary. Likewise modifying the defect density can influence the magnitude and dynamics of the process^{11,12,13,14} and most routes to prevent these photo-induced changes^{4,5,15,16,17,18,19,20,21} are associated with the blocking of migration routes. The microstructure of the material also determines the dynamics of the process, where the presence of grain boundaries (GB) has been shown to promote the photophysical changes^{5,22,23,24} and thus large crystals tend to be more stable. This matches with reports of the formation of I-rich domains at GBs^{23,25,26} although it has been shown that they can also appear throughout the bulk.^{27,28} On the other hand, when

the dimension of the material is reduced down to the nanometer scale photophysical changes are largely suppressed.^{29,30,31}

The general consensus is that mLHP films contain an initial distribution of entropically mixed halides. Due to the presence of a miscibility gap at room temperature³² external stimuli provide the driving force for halide ions to move from their original position leading to the formation of I-rich domains. Several proposals have been presented as the driving force for such structural changes, ranging from the electrostatic interaction between charges trapped at defects and spontaneously formed I-rich domains,²⁰ the presence of positive²² or negative²¹ charges at grain boundaries, a photo-induced strain gradient created by a uneven charge carrier generation pattern¹¹ or local strain induced by the formation of large polarons.²⁶

In this work we present a photophysical study of mLHP where the dynamics of the spectral changes are extracted locally and correlated with defect density. We find that the formation of I-rich domains extends well beyond the photo-irradiated regions and follows a complex behavior where structural changes within single crystalline grains and across grains have to be taken into account. Finally, the sample stoichiometry is modified by varying the halide-to-metal ratio, in order to elucidate the nature of the defects behind the process, finding evidence that supports that iodide-based defects are the ones playing a key role in the process. The present study highlights the need for local probes in order to correlate the many factors influencing the instability of mLHP. Further it unveils the complexity of this process which represents an extreme case of one of the main issues for LHP commercialization, that is photo-induced changes under external illumination.

The study of photo-induced changes in mLHP was carried out on $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{0.17}\text{Br}_{0.83})_3$ films. Details on sample fabrication can be found in Section S1.1 of the Supplementary

Information (SI). In an initial step we measured the PL from the samples using a combination of a CW ($\lambda=450\text{nm}$, $0.01\text{W}/\text{cm}^2$) and a pulsed ($\lambda=450\text{nm}$, $0.01\text{W}/\text{cm}^2$, 100fs pulses, 1kHz repetition rate) laser (Section S1.2 of the SI). In a typical experiment the sample is initially illuminated with the pulsed laser and only the PL peak associated with the mixed phase –Peak 1– is observed (Stage I in Fig.1), evidencing the absence of photo-induced changes as previously observed with low repetition rate sources.³³ Next the CW beam is introduced and a reduction in the intensity of the initial PL peak is accompanied by the emergence of a redshifted component –Peak 2– associated with the formation of I-rich regions (Stage II) with a composition of $\text{Br}_{0.2}\text{I}_{0.8}$ (see S1.3 and Fig. S1 in SI). Upon removal of the CW beam the sample returns to its original optical response over a longer period (Stage III).

Figure 1. Color plot showing the time evolution of the PL from a $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{0.17}\text{Br}_{0.83})_3$ film when illuminated with a pulsed kHz laser (Stage I), the combination of pulsed and CW laser (Stage II) and finally the pulsed laser again (Stage III). Right panel shows normalized PL spectra at the end of Stage I (red) and Stage II (black curve) where Peak 1 (2) from mixed (I-rich) phases are highlighted.

Control measurements were carried out to evidence that the pulsed laser does not introduce any photo-induced change (see section S2, Fig.S2 and Fig.S3 in the SI) and serves to give qualitative information on the composition of the film during the light induced changes (see Fig.S4). Further, small (below 3nm) spectral changes in Peak 1 during Stage II in Fig.1 evidence that the composition of the majority mixed-phase barely changes pointing to the absence of a phase in which the proportion of Br is larger than the stoichiometric 83% expected (see discussion in section S2 in the SI and Fig.S4). As the amount of I-rich material formed upon irradiation has been estimated to be in the 5-20% vol. range^{7,29,34}, the lack of a Br-enriched component indicates that photo-induced changes are actually triggered by a local rearrangement of iodide atoms where iodide vacancies and interstitials recombine, leading to an I-richer lattice.

Next we performed a local PL study using a laser scanning confocal microscope (LSCM) with spectral detection (see Section S1.4 in the SI for details). Figure 2 shows true-color PL images, each corresponding to a line scan of the region under study, together with PL spectra at different times showing a similar evolution to that in the macroscopic measurements of Fig.1. The initial image of the sample ($t=0s$) presents an inhomogeneous distribution of the PL intensity, which can be associated with a distribution of crystalline defects introducing intra-gap states responsible for non-radiative recombination paths for the photogenerated carriers.³⁵ PL spectra collected at different points of the image show a similar spectral position indicating an identical Br/I ratio across the sample (see section S3 and Fig.S5 in the SI). The spectra in Fig.2b and 2d were fitted to a double Gaussian and the time evolution of Peak 2 was retrieved to illustrate the dynamics of the process of formation of I-rich regions. The time evolution of I_{Peak2} could be fitted to a single exponential growth/decay from which a rate k_{growth} (k_{recovery}) of 0.017 ($0.011s^{-1}$) is obtained (see section S4 and Fig.S6).

Figure 2. True color PL images and spectra for a mLHP film tracking its evolution during irradiation (a,b) and recovery (c,d). Scale bars in all PL images correspond to 5μm. Grey (black) curves correspond to experimental data (fit to two Gaussians).

From the PL images in Fig.2a it becomes clear that regions with low initial PL intensity (i.e. high defect density) undergo a faster transition to a PL dominated by I-rich domains. To further establish this correlation, we extracted the dynamics of the photo-induced changes across a domain, comprising bright and dark regions (Fig.3). Plotting the time-evolution of the spectral response for a dark (Fig.3a) and a bright (Fig.3b) spot we see how the transition to a PL dominated by I-rich regions is faster in the former. To better appreciate this correlation, the spatial variation of the optical response across a domain (Fig.3e) was obtained. The Peak 1 intensity (Fig.3d) was extracted and compared with the activation constant, k_{growth} (Fig.3e), retrieved from the time evolution of Peak 2 at

each location. The spatial variation of the PL from the mixed phase is clearly the inverse to that of the dynamics of the photoinduced process.

Figure 3. PL as a function of time from a small domain in a $CH_3NH_3Pb(I_{0.17}Br_{0.83})_3$ film.

(a) Color plot showing the time evolution of the PL from a dark region where the I_{Peak2} is shown in the top panel. (b) Same data for a bright region. (c) True color PL images of the domain under consideration for three illumination times (scale bar is 1 μ m). (d) and (e) show initial I_{Peak1} from the mixed phase and growth rate of the I-rich I_{Peak2} respectively across the dashed line in (c). Point 1 and 2 correspond to those from which spectral information is shown in (a,b).

Establishing a similar trend for the recovery is not straightforward. While initially dark regions show a slower recovery, now the PL from the area under consideration (see Fig.2c) shows an additional spatial inhomogeneity with material recovery taking place at a faster pace for regions far from the image center. The combination of both dynamics determines the sample spectral behavior during the recovery. This radial distribution is not associated with the illumination pattern, which takes place through a sequential line scanning confined within the measurement area shown in Fig.2a and 2c. It likely points to structural changes extending beyond the illuminated area. This was confirmed by performing an irradiation cycle similar to that of Fig.2a, then opening the field of view of the microscope and collecting a series of PL images (Fig.4). Here it can be clearly seen

how the formation of I-rich domains associated with the migration of halide ions extends beyond the illuminated area (see section S5 and Fig.S7 in the Supplementary Information), pointing to a long-range driving force as will be discussed below.

Figure 4. Expanded confocal PL images taken after irradiating the region highlighted by the dashed line. Images were taken after 0.5 (a), 1 (b) and 3 (c) minutes.

To further explore the nature of the defects behind these changes we fabricated a set of samples where the composition was changed by keeping the Br/I mol ratio constant but varying the halide-to-metal ratio $R_H = (n_{Br} + n_I)/n_{Pb}$ above and below the stoichiometric value $R_H = 3$ in order to modify the density of halide-related defects. Details on film fabrication are given in section S1 of the SI. Energy dispersive spectroscopy (EDS) measurements show that the samples have a slightly lower ratio (R_H^*) than the one contained in the precursors (see Fig.S8).

Next the PL from these samples was collected following illumination/recovery cycles as the ones shown in Fig.2 on $20 \times 20 \mu m$ regions. Figure 5a shows the initial Peak 1 intensity (corresponding to the mixed phase) of the samples after the first laser scan for different values of R_H^* , showing a monotonic increase pointing to a reduction in the density of defects introducing deep-trap states, which have been associated with halide interstitials and lead vacancies in the bulk [36] as well as at GB.³⁷ In principle one would expect that increasing R_H should rise the density of halide interstitials. To solve this apparent contradiction we next consider the spectral response of Peak 1 (Fig.5b) and observe how

increasing R_H^* leads also to a slight redshift pointing to a larger fraction of iodide incorporating into lattice positions. This trend was also observed when studying the synthesis of the films of different stoichiometry with XRD (see Section S6.2 and Fig.S9 and S10 in the SI). These evidences indicate that as R_H rises, the total amount of halide in the sample increases but in a different manner depending on its nature. Iodide incorporates into lattice positions, as indicated by PL and XRD results. On the other hand, additional bromide would incorporate either as interstitials or as part of an amorphous phase.

Next the growth/recovery rates of Peak 2 were extracted for samples with different R_H^* (Fig.5c). We see how k_{growth} drops with R_H^* which, according to the above discussion, implies that it is iodide defects that most influence the photo-induced changes in mLHP films. This can be explained as vacancies have been demonstrated to be the main route for halide migration in LHP³⁸ and also for the formation of I-rich domains in mLHP,¹⁴ albeit halide migration through interstitials has also been shown to be relevant for LHP.^{39,40,41,42}

Finally the recovery rate $k_{recover}$ of the optical response of the different films shows an inverse trend to that of k_{growth} , increasing as R_H^* grows (Fig.5c). Such recovery, as shown in Fig.2c, takes place following a completely different spatial pattern with a radial distribution of the spectral changes pointing to a movement of ions across domains. Upon observation under scanning electron microscopy (SEM) it can be appreciated (Fig.S11) that decreasing R_H influences the sample morphology, where the connectivity between domains is increased as the halide-to-metal ratio rises. Assuming inter-domain migration to take place through GBs would agree with recent reports of these extended defects behaving as efficient routes for ion migration.^{43,44}

Figure 5. Evolution of the initial Peak 1 intensity (a) and spectral position (b) of a mLHP film as well as the rate of growth/recovery of Peak 2 (c) with the halide-to-metal ratio R_H^* estimated from EDS.

According to the results presented herein the driving force behind the formation of I-rich domains needs to have a long-range spatial extent in a direction normal to that of the incident pump beam. This matches with the diffusion of photo-generated charges, either as free carriers or as large-polarons,⁴⁵ which have been reported to span values from a few microns to above 100.^{46,47,48,49,50} Further, the presence of defects promotes the formation of I-rich regions which matches the mechanism of carrier trapping proposed in Ref. 20 but also could favor the formation of large polarons.⁵¹ In particular we have seen that it is iodide related defects that would have a combined role of trapping charges and providing the main migrating species, matching with recent reports pointing at this element as the most mobile species under illumination in mLHP.⁵² Thus under light illumination the crystalline lattice would be partially repaired mainly by the formation of

regions where iodine vacancies/interstitials recombine leading to the formation of I-rich regions (see Scheme 1). This would agree with the absence of a Br-rich phase observed by us and others. Nevertheless, the presence of Br-rich regions reported in the literature is also feasible if the synthesis leads to i.e. a majority of initial Br-related defects. The relevance of morphology and defect structure is likely related to the recent observation of intermediate I-rich regions.⁵³

Scheme 1: Proposed mechanism responsible for photoinduced phase segregation. An initial distribution of halide interstitials and vacancies is modified under external illumination leading mainly to the recombination of I-related defects ending up in the formation of I-rich regions.

Finally, upon removal of the external illumination, the system returns to its original configuration driven by entropy. At a local level, initially defective (dark) regions that underwent pronounced photo-induced changes take longer to return (Fig.2b). On a macroscopic scale, the recovery dynamics are dominated by a radial pattern, evidencing an inter-grain ionic migration strongly linked to the sample domain connectivity, likely taking place through GBs where enhanced ion migration has been reported.^{43,44} This shows that, while most photophysical experiments on mLHP are performed on a macroscopic scale, a correct interpretation requires taking into account the sample morphology as it strongly determines phase segregation through an interplay of bulk and GB processes.

In summary, a local photophysical study of mLHP films has been carried out where a direct correlation between defect density and I-rich region formation has been established. Employing local photophysical characterization on samples with different stoichiometry, we have found evidence that it is iodide-related defects that play a key role in the process. Further, the extent of the observed changes, which occur far beyond the illuminated region, point to photo-generated charge carriers, either as free carriers or in the shape of large polarons, which would be responsible for the driving force as they are trapped by defects. Finally, the recovery dynamics point to a complex scenario where combined inter and intra-domain processes, strongly dependent on sample morphology, are taking place. These results explain the origin of the process that gives rise to the conspicuously observed phase segregation of mixed halide perovskites and reveal that a precise knowledge of the sample morphology and defect structure is needed to disentangle the contribution from different atomic components and their migration routes. The relevance of the present work further relies in the fact that phase segregation in mLHP is a part of a broader issue comprising the photo-induced halide migration whose mitigation is fundamental for future applications.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

Experimental (Film fabrication, PL spectroscopy experiments, Estimation of composition from I-rich domains, Laser scanning confocal microscopy (LSCM) experiments); PL spectra from mLHP films; Spectral homogeneity in confocal images; Growth/recovery dynamics; Spectral information from the region surrounding the

illuminated area; Films with different stoichiometry (EDS studies, Film formation, SEM).

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Author Contributions

The authors declare no competing financial interests.

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