Improving the Bulk Emission Properties of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ by Modifying the Halide-Related Defect Structure

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ABSTRACT:

The peculiar defect chemistry of hybrid organic-inorganic lead halide perovskites is believed to be partially responsible for the outstanding performance of this solution processed material in optoelectronic devices. While most effort has been put on the management of halide defects (the ones presenting the highest mobility) for $\text{CH}_3\text{NH}_3\text{PbI}_3$, its bromide counterpart has not been so widely studied. While the former is the material of choice for photovoltaics the latter is present in most light-emitting applications. Here we report how the exposure of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystals to a bromine atmosphere strongly affects its emission properties. Such improvement takes place in the absence of apparent signs of degradation and remains for tens of hours. We propose an explanation based on the defect structure for this material where bromine-related defects can act as deep or shallow traps. These results are of relevance for a material expected to be present in a new generation of solution-processed light emitting devices.

1. Introduction:

The nature and concentration of crystalline defects in a semiconductor strongly determines its performance from the point of view of its use in an optoelectronic device.¹ While intentional dopants can introduce an appropriate amount of shallow traps changing the nature of the majority carriers, defects leading to the appearance of deep traps within the semiconductor bandgap introduce non-radiative recombination paths for charge carriers which hamper its use in an optoelectronic device. For hybrid organic-inorganic lead halide perovskites, a material that over the past few years has shown great potential in several optoelectronic applications from photovoltaics² to light emission³ or detection,⁴ the nature, concentration and effect on material properties of defects is being actively studied.^{5,6} For this family of perovskites most devices are fabricated following a low temperature solution process approach, thus large densities of structural defects are expected to be created during its synthesis. Nevertheless, the excellent performance of these materials in optoelectronic applications points towards a high tolerance to the presence of such structural imperfections.⁷

For the particular case of $\text{CH}_3\text{NH}_3\text{PbBr}_3$, highly relevant for emission applications due to its bright emission in the green, several works have reported a wide range of values for the defect density in this material. While experiments relying on electronic contacting have presented extremely low densities in the 10^8 - 10^{10} cm^{-3} range,^{8,9,10} close to the values expected for inorganic semiconductors commonly employed in commercial optoelectronic devices, estimations from optical measurements have led to much larger values in the 10^{13} - 10^{16} cm^{-3} range.^{11,12,13} Beyond the role played by the sample morphology, where polycrystalline thin films are expected to host a larger density of defects than single crystals, the method used to estimate the defect concentration could also affect the value obtained¹¹ In this sense, the characteristic high

ion mobility in this kind of materials¹⁴ could influence the results when using electronic contacting. Further, in the presence of light illumination halide mobility within the perovskite lattice has been shown to increase due to the formation of bromine vacancies (together with associated interstitials) which can lead to additional deep-traps and non-radiative decay paths.¹⁵ While the expected depletion in material PL due to the introduction of these defects can be partially compensated upon illumination in the presence of an O₂ rich atmosphere,^{16,17,18,19,20} additional means to improve the material emission are needed. In this sense different post-fabrication treatments have been employed to reduce defect trap states in lead-halide perovskites. These approaches have been mainly oriented towards the passivation of traps present at the surface and grain boundaries of perovskite crystals, expected to introduce non-radiative recombination paths, by performing surface treatments.^{21,22,23,24,25,26,27,28,29,30,31}

In this work we propose a post-fabrication treatment intended to both improve the photoemission intensity throughout the entire volume of CH₃NH₃PbBr₃ micron sized single crystals and study the nature of trap states, related to the halide component of the perovskite matrix. This represents the first approach aiming at reducing the density of deep-trap states within the material volume and not only those related with surface traps. In particular we expose the perovskite crystals to a halide vapor and monitor its optical response. Spatial, spectral and time-resolved information is gathered to evidence the changes in material emission. Contrary to previous results on CH₃NH₃PbI₃, where exposure to iodine vapor leads to PL quenching, we report a dramatic improvement in the material emission lasting for tens of hours. The possible origin of these changes is discussed in terms of the defect chemistry of this material and the modification of the defect structure within the crystalline lattice when exposed to the halide vapor.

2. Methods:

2.1 Optical characterization: The proposed post-fabrication treatment was carried out on $\text{CH}_3\text{NH}_3\text{PbBr}_3$ micron sized single crystals fabricated following an already published procedure.³² Platelets with $1000\text{s } \mu\text{m}^3$ dimensions were placed in a sealed chamber through which a constant dry-air flux (ca. $4 \text{ l/s}\cdot\text{m}^2$) was passed. The chamber was placed in an inverted microscope where the optical response of the crystals was studied using a long working distance (WD=4.7 mm) 100X objective with numerical aperture NA=0.75 (PL FLUOTAR-L from Leica). Individual crystals were illuminated with a pulsed laser delivering 900ps pulses with $\lambda=450\text{nm}$ and $0.3\text{W}/\text{cm}^2$ intensity. The PL from the crystal was sent through three ports, one leading to a fiber coupled spectrophotometer (USB2000 from Ocean Optics) to collect its spectrum, another coupled to a time-correlated single photon counting (TCSPC) set-up to obtain the PL decay (selecting all emission above $\lambda=532\text{nm}$ with a passband filter) and another coupled to an EMCCD (Luca from Andor) where a PL image was collected at 532nm (selected with a notch filter).

2.2 Bromine flux: Samples were placed in a sealed cylindrical plastic chamber (height=2.8cm, radius=4.25cm) with entrance and exit apertures (diameter: 1.5mm). In order to expose the sample to a bromine flux the initial dry-air flux ($3.5\cdot 10^{-4} \text{ l/s}$) was passed through a 500ml gas washing bottle where a saturated bromine atmosphere was created by placing 500 μl of pure (Alfa Aesar, 99.8%) liquid bromine. As water is known to strongly affect the photophysics of hybrid perovskites we made sure it was absent from the experimental environment by flowing the dry gases during 5 minutes prior to introducing the bromine or illuminating the samples.

3. Results and discussion:

After an initial 2 minute illumination period, enough for the sample to be photo-activated and reach a stationary PL,^{16,17,18} bromine was introduced in the flux as described in the previous section. After a 60-80s period under the bromine flux the sample PL underwent a dramatic enhancement which ranged from 125-420% depending on the crystal under examination. Once the PL becomes stationary the bromine flux is replaced by dry-air again. Figure 1a shows the evolution of the maximum of the PL from a micro-crystal (SEM image shown in the inset of the Figure) during the air-bromine-air flux change. Here three regions can be distinguished comprising the initial photo-activation (I), PL enhancement during bromine exposure (II) and further PL stabilization upon returning to an air atmosphere (III). PL images collected by an EMCCD camera at 100s and 700s (Fig.1b and 1c) show the spatial distribution of the emission before and after exposure to the bromine flux. While initial PL maps show an inhomogeneous emission distribution³³ the final images evidence an overall enhancement. Fig.1d shows the spatial distribution of the PL enhancement (final minus initial images) showing how it takes place mainly within the central part of the crystal. Finally the sample was imaged in a Field Emission Scanning Electron Microscope (FE-SEM) (Zeiss Auriga). Here compositional information was obtained from energy dispersive spectroscopy (EDS) (see Section S1.1 and Fig. S1) and the ratio between Pb and Br %wt. led to the stoichiometric values expected for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (1.159) for bare samples and those exposed to the Br flux.

Figure 1. (a) Time evolution of the maximum PL from a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single microcrystal (see inset) as it is illuminated under dry air (region I), bromine (II) and dry air again (III). (b) and (c) show EMCCD PL images of the sample emission before and after exposure to the bromine flux. (d) Differential PL image obtained from (b) and (c).

From the PL spectra collected just before the bromine flux ($t=100\text{s}$) is passed and after a several minute stabilization period in air ($t=700\text{s}$) we can observe how the spectral emission does not change upon activation (Fig.2a). Both spectra show an asymmetric shape with a main peak at 536nm and a low energy component which has been recently reported to be related with PL from the bulk of the crystal.¹² The fact that the overall shape of the spectra does not change upon activation points to a volumetric effect, as a surface-only modification would mostly affect the 536nm peak leaving the low energy component unaffected. Together with the spectra, PL decay curves were collected for the sample before and after exposure to the bromine flux (Fig.2b). Here we can see a reduction in the lifetime extracted from the fit as we change from dry air ($\tau=1.51\pm0.03\text{ns}$) to bromine ($\tau=0.79\pm0.01\text{ns}$). These values are similar to those obtained

in the past for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystals having these dimensions.^{34,35,36} This trend was observed over many different crystals presenting different degrees of activation under a bromine flux (see Fig. S3 and Section S2 in the Supplementary Information).

Figure 2. (a) Normalized PL spectra of a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystal taken before (black) and after (red curve) being exposed to the bromine flux. (b) PL decay measurements (points) and fit to a single exponential (curves) for the same crystal before and after exposure to the bromine flux. Color code is the same as in (a).

In order to gain further insight into the mechanism through which the bromine flux is affecting the sample PL we collected a series of images during the activation of one crystal and performed an analysis in order to extract the spatial distribution of the PL activation dynamics. Figure 3a shows a typical PL image of a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystal and Fig. 3b the temporal evolution of the maximum of its PL at a certain point. Here we can observe an initial time interval t_0 where the PL remains unchanged before experiencing a rise which can be fitted to a bounded exponential growth with activation

time τ_{act} . Fig. 3c and 3d show the spatial evolution of t_o and τ_{act} during the activation of the sample. Here a clear trend can be seen where both quantities increase towards the center of the crystal, albeit more markedly for the case of the activation time. As with the PL spectra before and after exposure to the bromine flux (see Fig.2a), this behavior points to a volumetric effect. Here the effect of the bromine takes a given time t_o to appear, increasing towards the center of the crystal, as it has to diffuse towards the interior of the sample. Analogously, the activation dynamics (characterized by τ_{act}) in the presence of bromine slows down towards the center of the platelet, as expected due to the fact that bromine has to diffuse and its concentration is expected to decrease along this direction.

Figure 3. (a) PL image of a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystal. (b) Activation curve upon exposure to the bromine flux at a point on the sample. t_o and τ_{act} mark the time before PL enhancement starts and its activation time; the blue line is a fit to a bounded exponential growth. (c) and (d) show spatial maps of t_o and τ_{act} respectively (white

dashed line marks the crystal edges). (e) and (f) show the spatial variation of t_o and τ_{act} along the region marked by dotted lines in (c) and (d).

Once the sample PL has reached a maximum, the bromine flux is stopped and a dry-air flux is restored to remove any residual halogen gas within the chamber. The PL of the crystal is monitored after some time in order to study the permanence of the activation effect. Figure 4 shows the evolution of both, the PL intensity as well as the decay rate. Here it can be seen how the PL intensity undergoes a further increase (ca. 30%) in the first hour following exposure to the bromine vapor and then slowly returns to its initial value over a period of 70 hours. The PL decay rate also returns to the initial value over a similar time span. Finally, since the surrounding atmosphere has been demonstrated in the past to be a key factor in the photophysical properties of lead-halide perovskites^{16,17,18,19,20}, we have studied how it affects the activation upon a bromine vapor treatment. The PL enhancement was observed even in the absence of irradiation. For this, the PL of one crystal was monitored during bromine exposure and the PL of nearby crystals (not illuminated during the bromine treatment) was measured before and after the treatment, showing all of them a PL activation of different magnitude. In order to evaluate the effect of the atmosphere experiments were carried out where a N_2 flux instead of dry-air was used to carry the bromine vapor towards the sample chamber. Similar PL activations were observed (see Fig.S4 in the Supplementary Information) pointing to a negligible role of the surrounding atmosphere when a halogen vapor is present.

The effect of exposing organic-inorganic lead halide perovskites to halide vapors has been recently studied from an experimental^{37,38,39,40} as well as theoretical point of view⁴¹ for the case of $CH_3NH_3PbI_3$. The dissociation of an iodine molecule can lead to the

filling of a vacancy and/or the introduction of an interstitial. Both of these processes introduce holes and contribute to the p-doping of the material^{38,39} and decreases ionic conductivity, as it has been shown to be mediated through iodine vacancies.³⁹ Together with these effects, strongly affecting ionic/electronic conductivities, exposure to iodine vapors has also been shown to lead to sample degradation³⁷ and PL quenching.⁴⁰ In our case, during the time needed for PL activation, the sample presented no sign of degradation as evidenced by X-ray diffraction (XRD) measurements (see Fig.S5). Longer times, of several minutes, under the halide flux were needed to start appreciating the first signs of degradation in the form of a drop in emission from the single crystals (see Fig.S6).

Figure 4. Evolution of the PL intensity (a) and decay rate (b) of a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystal after it has been exposed to a bromine flux for a 2 minute interval (grey box). Dashed horizontal lines show the initial value of both magnitudes before exposure to the halide vapor.

In order to account for the observed PL enhancement, not reported in any of the above mentioned works dealing with $\text{CH}_3\text{NH}_3\text{PbI}_3$, we have to consider the defect structure of

the material under consideration. While several works have studied theoretically by means of Density Functional Theory (DFT) the defect chemistry in $\text{CH}_3\text{NH}_3\text{PbI}_3$,^{42,43,44,45,46} fewer have done so for the bromine counterpart. Buin and co-workers showed⁴⁵ that while bromine vacancies are more probable to be present than interstitials (regardless of whether bromine rich or poor conditions are considered) only the former are expected to introduce deep trap states that contribute to the non-radiative recombination of photo-generated carriers and will thus lead to a quenching of its PL. As the dissociation energies for I_2 and Br_2 are comparable (152kJ/mol y 192kJ/mol) when exposed to a bromine atmosphere one would also expect, as in the case of $\text{CH}_3\text{NH}_3\text{PbI}_3$, the filling of vacancies and the introduction of additional interstitials. Since the latter represent shallow defects that do not contribute to PL quenching, the overall effect would be a reduced density of deep trap states and therefore an enhanced PL intensity in accordance with the results presented. Together with the filling/creation of vacancies/interstitials upon exposure to Br_2 vapor one could also expect the onset of material degradation taking place as a consequence of interaction of bromine species with the organic cation as suggested for $\text{CH}_3\text{NH}_3\text{PbI}_3$ in Ref. 37. This would be responsible for the PL quenching observed for prolonged exposure times.

If non-radiative recombination paths are reduced, given by the filling of bromine vacancies upon exposure to the halide vapor, one would expect a reduction in the measured decay rate evidencing the decrease in the overall decay paths. This fact is at odds with our observations (see Fig.2) where an enhanced PL is accompanied by faster decay rates. To account for this one has to take into account that together with a reduction in the number of non-radiative decay paths we are increasing the hole concentration which directly affects the PL dynamics⁴⁷ and has been shown to reduce the PL lifetime for the case of $\text{CH}_3\text{NH}_3\text{PbI}_3$.³⁸ Thus by exposing the $\text{CH}_3\text{NH}_3\text{PbBr}_3$

single crystals to bromine vapor we would be promoting both mechanisms, reduction of deep traps and p-doping of the material, which have opposite effects on the PL decay rate and hence one could expect a net reduction in PL lifetime.

Finally, in order to account for the directional enhancement of the PL starting at the sample edges and moving towards the center (Fig.3) one has to bear in mind that, as shown by numerical simulations⁴¹ for the case of $\text{CH}_3\text{NH}_3\text{PbI}_3$, the dissociation of the halide molecule present in the atmosphere can be strongly facet depending (more favorable for the (100) planes in the case of $\text{CH}_3\text{NH}_3\text{PbI}_3$ exposed to I_2). In this sense, the fact that t_0 presents a plateau-like spatial behavior with shorter values at the edges (see Fig.3c and 3e) could indicate a less favorable dissociation rate for those planes present at the sample surface, (100) as shown by the XRD, than those at the edges, probably (111) or (110) present where two (100) planes meet. Such directional dependent interaction with the atmosphere is likely related with the fact that the crystal edges emit more efficiently (see Fig.3a) and degradation upon prolonged irradiation also starts there as reported in Ref. 33, evidencing that the interaction of the sample with the surrounding atmosphere strongly depends on its crystallographic termination. This last point has also been suggested by first-principles calculations where the crystallographic termination of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was shown to strongly determine its stability.⁴⁸ Again, similar studies for the case of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ will be needed to further understand the highly directional emission properties mentioned above.

4. Conclusions:

To conclude, the interaction of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystals with bromine vapor represents a means to further understand and manage its defect structure, improving the PL

properties of a material which is called to play a key role in optoelectronic applications dealing with light emission. While such improvement opens the door to post-synthetic paths to address the bulk defect structure of this type of lead-halide perovskites further work will be needed to fully understand the processes behind the observed changes. Thermodynamic calculations like those carried out for $\text{CH}_3\text{NH}_3\text{PbI}_3$ in Ref. 41 could shed some light on certain aspects such as the reversibility of the process, as any treatment intended for enhancing the material emission with potential to improve device performance will certainly need more durable results. Previous work dealing with the iodine counterpart only studied the permanence of p-doping for 10 hours upon I_2 exposure. Also the strongly facet-depending dissociation of I_2 molecules at the $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface could explain the strong effects observed in our single crystals with (100) planes exposed to the atmosphere. Nevertheless, the possibility of improving the material emission in the absence of any appreciable degradation represents an exciting prospect for future work.

Supporting Information.

Experimental (optical characterization, bromine flux, SEM and EDS, XRD). Lifetime measurements over different micro-crystals. PL changes under bromine flux combined with inert gasses. XRD study of activated sample under bromine flux. Study of sample degradation under prolonged bromine flux. (PDF)

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Notes

The authors declare no competing financial interests.

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TOC Graphic: