

Nanoscale investigation of organic – inorganic halide perovskites

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Abstract. Over the last few years organic – inorganic halide perovskite-based solar cells have exhibited a rapid evolution, reaching certified power conversion efficiencies now surpassing 20%. Nevertheless the understanding of the optical and electronic properties of such systems on the nanoscale is still an open problem. In this work we investigate two model perovskite systems (based on iodine - $\text{CH}_3\text{NH}_3\text{PbI}_3$ and bromine - $\text{CH}_3\text{NH}_3\text{PbBr}_3$), analysing the local elemental composition and crystallinity and identifying chemical inhomogeneities.

1. Introduction

Mixed halide perovskites represent an emerging and widely investigated class of nanostructured materials. Recent studies have shown that the inhomogeneous properties of these materials are related to the grains distribution of the thin film [1] but a better knowledge of the local chemical composition is required to shed light on the still unknown processes underlying the local recombination centres in the films. In this context, the use of analytical electron microscopy could play a key role in the determination of elemental distribution at the nanoscale. The recent technical improvements, such as the introduction of high-brightness electron gun and large area EDX detectors, result in fast acquisition and limited electron dose on the sample, a crucial factor in the study of an organic – inorganic compound. Here we present EDX elemental maps of model perovskite systems acquired in STEM mode, and analysed using multivariate statistical analysis methods. In addition, High Resolution TEM was used to study the presence and the dimensions of crystalline domains within the films and their possible connections to the optoelectronic properties measured by optical methods.

2. Materials and methods

Methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) were prepared according to standard procedure [2]. Bromine – based samples were synthesised following two different methods: using equimolar mixtures of methylammonium bromine ($\text{CH}_3\text{NH}_3\text{Br}$) and bromine iodide (BrI_2) and molar stoichiometric ratios of CH_3NH_3 and ($\text{Pb}(\text{CH}_3\text{COO})_2$) in 20 wt% N,N – Dimethylformamide (DMF).

The perovskite films were analysed in a FEI Nova NanoSEM and in a FEI Tecnai Osiris TEM operated in scanning (STEM) and HRTEM mode at an acceleration voltage of 200 kV. The microscope is equipped with Bruker's Super-X EDX detectors and a high brightness electron gun (X-FEG), resulting in high count rates for elemental mapping. Elemental maps were acquired over areas



of $8 \times 8 \mu\text{m}^2$, with sampling every 100 nm and a dwell time of 100 ms per pixel, using a beam current of 700 pA and a probe size of 1 nm in diameter, and analysed using Hyperspy [3], an open source Python library dedicated to hyperspectral data analysis. Samples for TEM analysis were prepared by transferring scratched perovskite films on a TEM grid.

3. Results and discussion

Initially the morphology of the films was investigated. It was found that the precursor used in the synthesis process strongly affects the morphology of bromine film. $\text{CH}_3\text{NH}_3\text{PbBr}_3$ samples, prepared using PbBr_2 as precursor, present the typical perovskite crystallite structure, with cubes several microns in size, whereas the lead acetate based perovskite exhibits a much more homogenous film (**Figure 1 a,b**). The morphology of the iodine based film is completely different and the presence of elongated structures is evident in **Figure 1 c**.

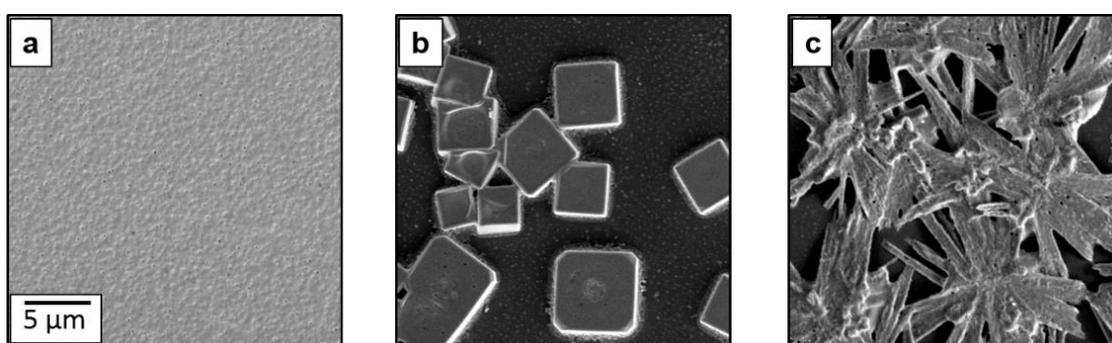


Figure 1. SEM images of a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ synthesized using acetate (a), $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (b) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ (c). The scalebar applies to all images.

High Resolution TEM was used to study the crystallinity of the films to complement morphological information gathered from SEM analysis. The materials present crystalline domains, bigger in the bromine than in the iodine samples. HRTEM images (**Figure 2**) show a polycrystalline structure with adjacent domains of different crystal orientation on a length scale of 10s of nanometers. Fast Fourier Transforms (FFT) of the lattice show spacings compatible with the unit cell of known hybrid perovskite structures [4]. The materials do not appear amorphous. From these results it is possible to hypothesize a correlation between the local variation in photoluminescence [1,5] and phase and orientation of the perovskite domains, within both the bromide and the iodide based perovskites.

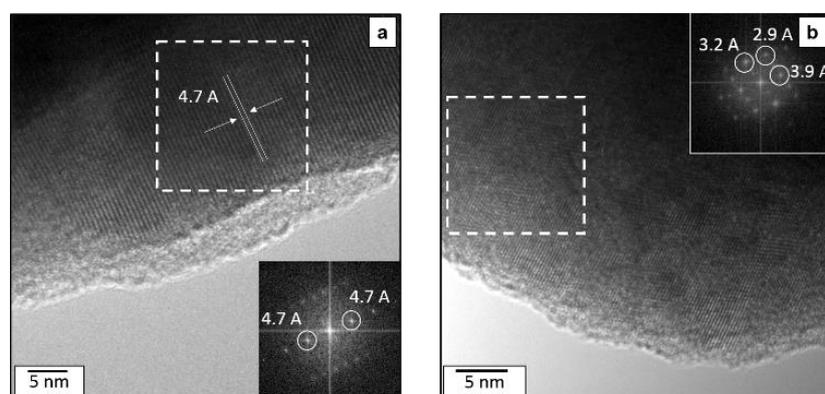


Figure 2. HRTEM images of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (a) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ (b) samples. The FFTs of the areas in the dashed squares are reported in the insets, with the visible lattice spacings highlighted. The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ sample presents larger crystalline domains and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film is polycrystalline.

STEM EDX analysis was performed in order to study the local chemical composition and to assess the relative differences in the elemental composition. EDX data were treated using a PCA (Principal Component Analysis) – based routine. A model of the raw data has been reconstructed using a limited set of components, omitting those that contain only noise. Cliff Lorimer quantification method was applied on the denoised spectra, obtaining EDX elemental maps with nm-level spatial resolution. As shown in **Figure 3** the differences between iodine and bromine EDX maps in both stoichiometry and homogeneity result quite clear. In the bromine based film the ratio Br/Pb is close to the nominal composition, whereas in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film the ratio is on average of the order of 1.2 and that is probably due to an incomplete conversion of the precursor in the synthesis process. The local variations in chemical composition are more evident in the pure iodine samples and I/Pb ratio varies between 0.92 and 1.36 in different regions. A detailed analysis to verify a direct link between photoelectronic properties and chemical variation is planned, and will be carried out in further studies.

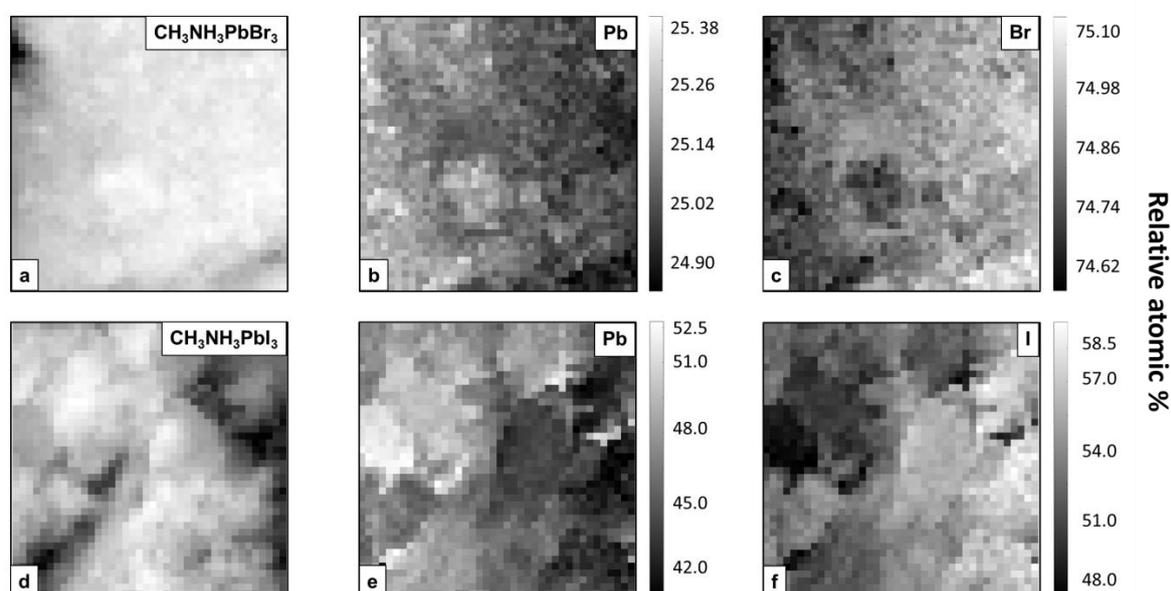


Figure 3. HAADF STEM images of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (a) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ (d). Elemental maps of Br (b), Pb (c,f) and I (e) are reported for the two samples. All images are $4\mu\text{m} \times 4\mu\text{m}$.

Although STEM and TEM are techniques that provide crucial information on the nanostructure of the materials, the interaction of the electron beam with the sample can cause temporary or permanent changes to the samples. These phenomena are dependent on the atomic number of the elements in the specimen, their bonding, the electrical and thermal conductivity of the specimen. In a mixed organic-inorganic perovskite system, it is possible that different components of the crystal will be sensitive to beam damage in different ways, with the organic components of the crystal losing mass at higher rate than the inorganic Z-number component. Since precise quantification of light elements is problematic using EDX, and the main focus of this study was the compositional analysis of the inorganic component of the perovskite films, we only investigated the variations of Br, I, Pb (Cu signal from the support grid can also be seen in the spectra). Beam damage was tested acquiring EDX maps on the same area of the sample, using an acquisition time of 20s, 120s and 20s and a dwell time of 100ms per pixel. The analysis was carried out on a mixed halide perovskite film, with a halide mixture having a nominal ratio bromine/iodine:40/60. As shown in **Figure 4** the chemical composition, after the acquisition of three spectra on the same area, does not change drastically.

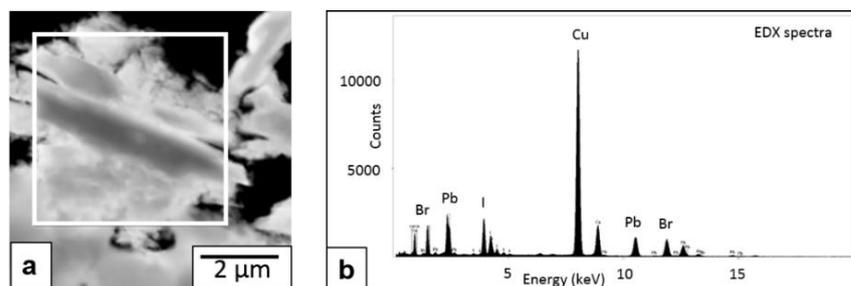


Figure 4. (a) STEM image of a mixed halide perovskite. The area in the white square has been analysed to test beam damage on the sample. (b) EDX spectrum of mixed halide perovskite after 20s of acquisition time.

Table 1. EDX spectrum quantification of mixed halide perovskite with an acquisition time of 20 s, 120 s and 20s. The quantification has been carried out using ES Vision

Element	Atomic % 20s	Atomic % 120s	Atomic % 20s
Cu(K α)	76.72	76.01	75.55
Br (K α)	08.82	09.64	10.01
I (L α)	07.22	06.41	06.14
Pb (L α)	07.22	07.93	08.16

4. Conclusions

Efficient elemental mapping in EDX-STEM allowed us to assess the chemical homogeneity of the inorganic component of Pb-Br and Pb-I perovskites, while high resolution TEM imaging demonstrated the nano-crystallinity of the materials. In particular, preliminary electron microscopy analysis shows that both orientation and phase of the crystallites and local elemental composition vary within the perovskite thin films.

In conclusion the use of STEM EDX analysis represents a powerful and versatile tool for the characterisation of devices based on hybrid composites with nano- and micro- scale structural and chemical features. Furthermore the latest developments in TEMs and data processing open up new opportunities for the investigation of optoelectronic devices, including beam sensitive materials, providing new information that can contribute to the understanding of the physical phenomena underlying the operation of solar cells, LEDs and lasers.

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