Unveiling the chemical composition of halide perovskite films using Multivariate Statistical Analyses

Stefania Cacovich[1§], Fabio Matteocci[2], Mojtaba Abdi-Jalebi[3], Samuel D. Stranks[3], Aldo Di Carlo[2], Caterina Ducati[1], Giorgio Divitini[1]

[1] Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom.
[2] Centre for Hybrid and Organic Solar Energy (CHOSE), University of Rome Tor Vergata, via del Politecnico 1, Rome 00133, Italy.
[3] Cavendish Laboratory, University of Cambridge, JJ Thompson Avenue, Cambridge CB3 0HE, United Kingdom.
Present Address: § Institut Photovoltaïque d'Île-de-France (IPVF) 30, Route départemental 128, 91120 Palaiseau, France.

Research into hybrid organic-inorganic perovskite solar cells (PSCs) has flourished over recent years, attracting strong interest by the scientific community. The global research effort associated with the rise of hybrid perovskites resulted in rapid advances in chemical formulation, fabrication methods and device architecture - however, most of the progress has been through empirical device improvements, and a number of key questions still remain unanswered. In particular, long term stability of the modules under operating conditions is considered to be the main drawback preventing commercial applications. However, poor stability not only prevents easy commercialisation - it also complicates scientific research: commonly used optical and analytical characterisation tools can induce reversible or irreversible structural/chemical changes in the perovskite films through the use of high energy photon or electron beams.

In this work we propose an approach that combines the acquisition of high-resolution chemical maps by scanning transmission electron microscopy (STEM) with dedicated MultiVariate Analysis (MVA) methods that improve signal/noise ratio (SNR) and identify correlations between the spatial distribution of elements. Such correlations emerge from statistical analysis and consist of maps that describe the distribution of chemical compounds rather than just elements. The use of methods that minimise operator input improves the reproducibility of results and the sensitivity to unexpected chemical compounds, such as phases with unpredicted stoichiometry, or elemental segregation. This approach is particularly valuable for hybrid perovskite-based films and devices, in which complex compounds can form, ionic species are prone to migration, and the electron dose during STEM analysis needs to be minimised to prevent local damage. Specifically, we tested and compared different computational methods - Principal Component Analysis (PCA) and Non-Negative Matrix Factorisation (NMF), demonstrating how they can be used to increase the SNR ratio of a dataset and provide new insights on the local chemistry [1]. The process flow is as follows: Initially, a cross-sectional sample is extracted from a solar cell (or a perovskite film) using conventional Focused Ion Beam (FIB) preparation and transferred to a (scanning) transmission electron microscope (STEM) [2]. STEM-EDX (Energy Dispersive X-ray spectroscopy) analysis is carried out using optimised illumination conditions to limit the electron dose on the sample, and the experimental data is processed using MVA algorithms available in open source scientific analysis packages such as python-based Hyperspy.

The same analytical approach can be used in the investigation of novel complex compounds, with particular benefits in materials and devices that are beam-sensitive or contain a variety of intermixed compounds. Additionally, decomposition can be a powerful tool in the investigation of dynamic processes – for example, for *in situ* measurements in the TEM: denoising routines allow the extraction of information from data acquired quickly and with poor SNR, whereas factorisation can directly track the emergence of new phases. Cross-sectional chemical characterization of a passivated perovskite thin film.
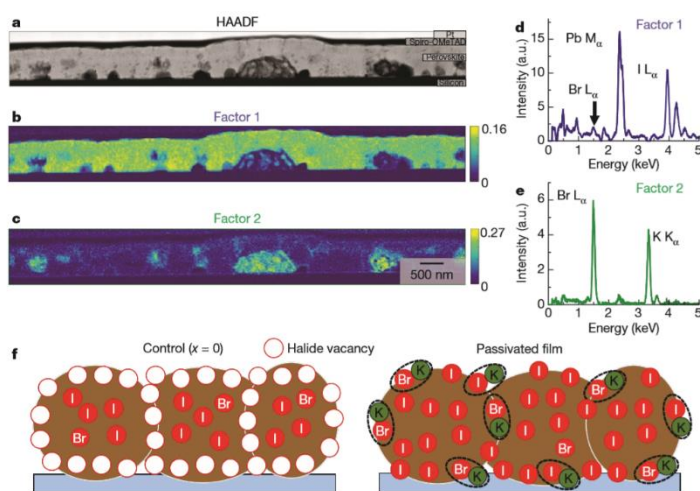

Figure 1. a, HAADF STEM cross-sectional image of a $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ potassium-passivated perovskite thin film. **b, c,** Analysis of STEM data using NMF decomposition reveals the presence of factor 1 (b), associated with the perovskite layer, and of factor 2 (c), which is rich in potassium and bromide. **d, e,** The EDX spectra of factor 1 (d) and factor 2 (e). **f,** Schematic of a cross-section of a film showing halide-vacancy management in cases of excess halide, in which the surplus halide is immobilized through complexing with potassium into benign compounds at the grain boundaries and surfaces. Adapted from [1].

1) Maximising and Stabilising Luminescence from Halide Perovskite with Potassium Passivation. M. Abdi-Jalebi, Z. Andaji-Garmaroudi, S. Cacovich, C. Stavrakas, B. Philippe, J. Ritcher, M. Alsari, E.P. Booker, E.H. Hutter, A.J. Pearson, S. Lilliu, T.J. Savenije, H. Rensmo, G. Divitini, C. Ducati, R.H. Friend, S. D. Stranks. *Nature*, 555 (7697), 497, 2018.
2) Unveiling the Chemical Composition of Halide Perovskite Films using Multivariate Statistical Analysis. S. Cacovich, F. Matteocci, M. Abdi-Jalebi, S.D. Stranks, A. Di Carlo, C. Ducati, G. Divitini. *Submitted.*