

Investigation of internal electric field in perovskite solar cells

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The observation of hysteresis behaviour occurring for current and photocurrent measurements of lead halide perovskite solar cells has taken the community by surprise. On one hand groups have tried to establish a reliable method to characterise devices to extract figures of merit related to solar cell functionality. On the other hand significant effort has been invested in trying to understand the origin of hysteresis and its potential connection with the outstanding performance of perovskite devices.

One of the most striking effects related to hysteresis of perovskite solar cells is that the optoelectronic properties of these devices show characteristic timescales which span over 10 orders of magnitude. The very slow transient behaviour is particularly surprising given the relatively high charge carrier mobility expected for these materials. The most accredited hypothesis is that variation of internal electrostatics influences the collection efficiency of the device and in general its response to optical and electrical stimulation. Different possible causes could underlie such process, among which slow detrapping of trapped charges and ion migration within the active layer of the device being the most plausible given the community's current understanding.¹ In both cases of ion migration or trapped charges, the dynamics of the changes in electric field could in fact occur in the second – hundreds of second timescale.

Regardless of the actual nature of the species responsible for changes in electrostatics within the device, measurements techniques that are able to probe the internal electric field of solar cells are of great interest and importance in this context. Spectroscopic techniques are particularly interesting because of the possibility to apply them in-situ and non-destructively.

We present electroabsorption (EA) measurements performed on perovskite solar cells. The collected EA signal relates to changes in optical transmission of the device upon application of an external voltage. Different possible physical phenomena contribute to changes of the optical properties in a semiconductors when applying an electric field. Shift of the electronic energy states (Stark effect) is expected for semiconductors, generally resulting in changes of its optical density with profile that follows the first or second derivative of the absorption coefficient. Stark effect-like features have been observed in the EA spectrum measured on perovskite active layers between TiO₂ and PMMA/Ag contacts and it was also hypothesised as an explanation for the electroreflectance signal measured for complete solar cells.^{2,3} A more recent study has shown that the EA features might instead be dominated by Franz-Keldysh effect.⁴

In our study we look at solar cells with 'standard structure' comprising an electron injecting contact deposited on FTO substrates at the bottom of the cell and a hole injecting material which is solution processed on top of the perovskite active layer. The cell is fabricated with conventional thickness of the active layer, but with only about 40–50 nm of gold used as top contact, in order to obtain sufficient semitransparency to perform transmission mode experiments. In our investigation we show square dependence of 2nd harmonic EA signal to applied voltage amplitude down to few hundreds of millivolts, suggesting linear proportionality between changes of potential at the electrodes and internal electric field in the perovskite layer. Moreover, we study the frequency dependence of the EA signal in the range 1Hz – 100kHz. We demonstrate that at low frequencies, variation in EA amplitude is observed for perovskite solar cell devices. We discuss this observation on the basis of the hypothesised ion migration process.

We consider device architectures which have previously shown differences in hysteresis. First, we address the effect of varying electron injecting material. Our group has recently reported that changes in surface recombination in the device affects the extent to which ion migration gives rise to current voltage hysteresis effects.⁵ Here we discuss other possible effects of changing the interface between the perovskite and charge collecting contacts based on EA

measurements. Secondly, we address the active layer composition and morphology on the dynamic response of the internal electric field to the applied potential. We show evidence that ion migration occurs in perovskite compositions which have been reported as “hysteresis free” and discuss possible reasons that could reconcile these contrasting observations. We finally discuss our spectroscopy results in combination with optoelectronic transient measurements where we consider the long time scale behaviour of the solar cells as a function of architecture. The effect of different prebiasing stages on the photocurrent evolution is used to quantify the device's hysteresis. We also discuss the possibility that multiple species cause the wide range of time constants observed from our measurements.

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