Where do ions migrate in perovskite solar cells, in the bulk or at the grain boundaries?

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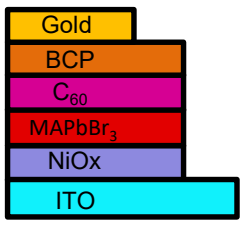
Motivation:

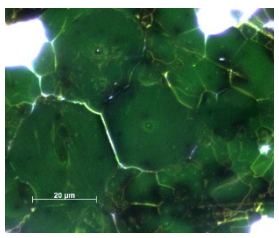
We compare ion migration in $MAPbBr_3$ solar cells with different grain sizes, which results in different bulk to boundary ratios.
Like this we can determine if ions migrate at the grain boundaries or inside the bulk.
The grain size is tuneable with the spin coating time.

Device architecture:

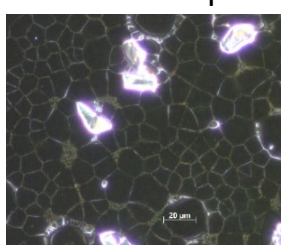


$MAPbBr_3$ solar cells with varying grain size:

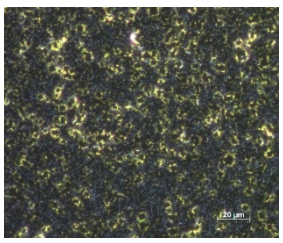
5 s: 20 µm



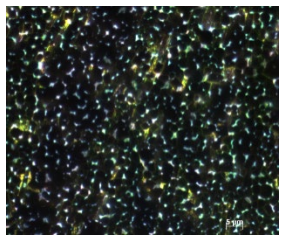
10 s: 10 – 20 µm



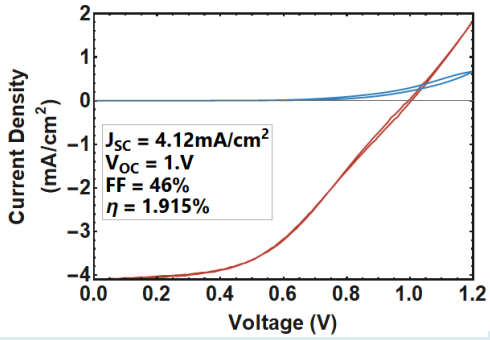
20 s: 3 – 5 µm



60 s: 2 – 3 µm

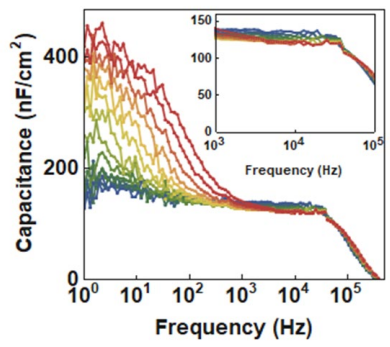


I/V curve:

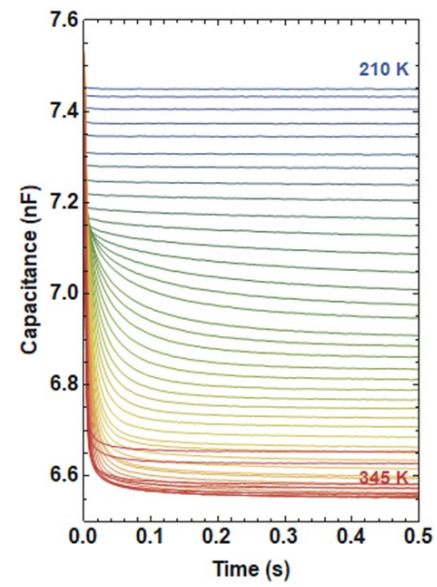


Impedance Spectroscopy /Transient Ion Drift:

We measure the capacitance after applying a voltage pulse for 2 s for a range of temperatures.
To quantify the Ion migration we fit every transient to an exponential decay.
With the help of an Arrhenius plot we can extract four parameters about the migration:



Capacitance transients for the 20 µm sample with a voltage pulse of 0.75V:

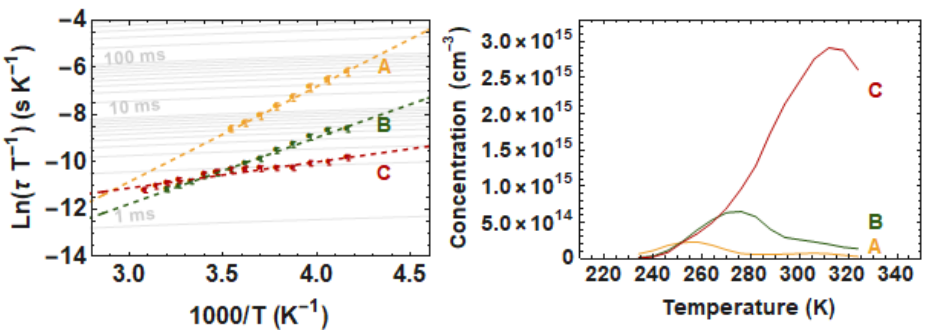


s : anion / cation
N_{ion} : density of mobile ions
D_0 : diffusion coefficient
E_A : activation energy

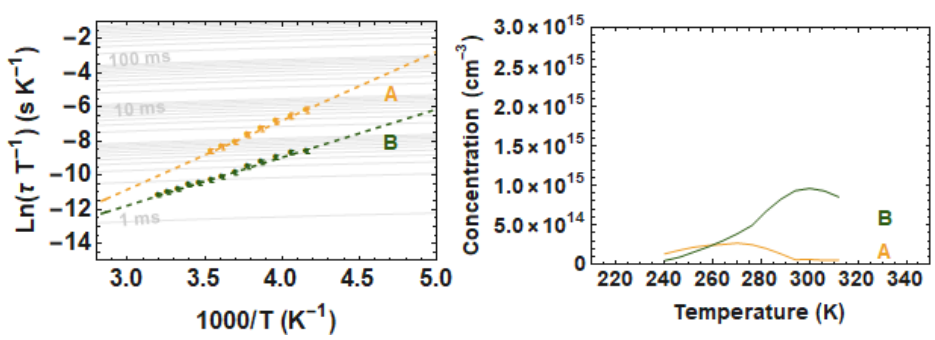
Futscher, M. H., Lee, J. M., McGovern, L., Muscarella, L. A., Wang, T., Haider, M. I., ... & Ehrler, B. (2019). Quantification of ion migration in CH 3 NH 3 PbI 3 perovskite solar cells by transient capacitance measurements. *Materials Horizons*.

Results and Discussion:

20 µm grain size:



2 - 3 µm grain size:



- all samples show a decay in capacitance which shows that there is only anion migration→ Br^--migration
- the large grain size sample (20 µm), has three different types of movement or pathways (A, B and C)
- the smaller grain size (2 – 3 µm) has only two different types of movements A and B
- for higher temperatures we found further features which can not be explained by Ion migration, we are currently speculating that these result from reactions taking place at the interfaces or contact layers

Acknowledgements NWO

Conclusion:

- all detected Ion migrations are resulting from Anion Movement → Br^--migration
- the smaller grain size shows one movement less than the larger grain sizes
- more research is needed to elucidate on the nature of the three migration types