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Detection and relevance of ion conduction in hybrid organic-inorganic halide perovskites for photovoltaic applications

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Detection and relevance of ion conduction in $CH_3NH_3PbI_3$ for photovoltaic applications

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MAX-PLANCK-GESELLSCHAFT

Non Stoichiometric Compound VI
Santa Fe (NM)
5-8 Sept. 2016
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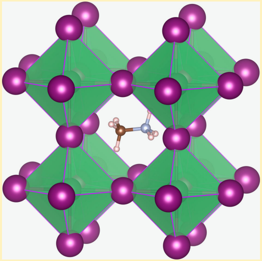
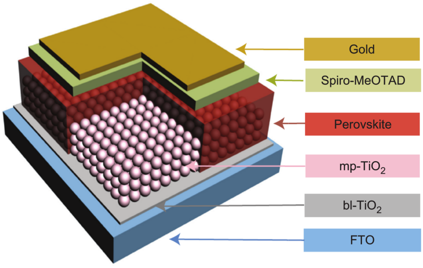
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

$CH_3NH_3PbI_3$ and Perovskite Solar Cells



Eames *et al.*, *Nat. Commun.*, **2015**



Li *et al.*, *Nature Chem.*, **2015**

- Direct $E_G = 1.5$ eV
- High absorption
- Low exciton bind. energy
- $\sim$100 μm diffusion lenghts[1]
- High PCE of > 22 %[2]

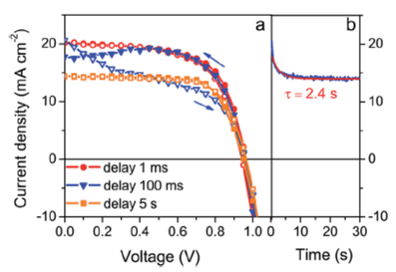
[1] Dong *et al.*, Science, **2015**, 347, 967-970.

- Anomalous behaviours
- Degradation (T, $P(H_2O)$)
- Low stability of devices
- Low reproducibility

[2] NREL National Center for Photovoltaics.

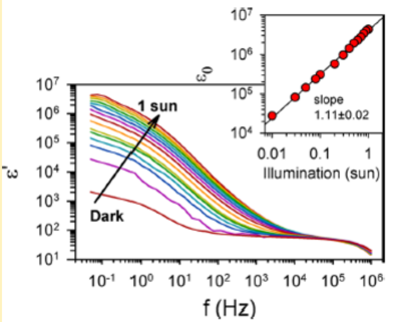
1. Expected concentration of ionic defect is high
2. Ionic defects related to stability
3. It can explains "anomalous" low frequency behaviours
4. Ionic defects influence on photovoltaic properties

Hysteresis in i-V sweeps



Unger *et al.*, *Energy & Environ. Sci.*, 2014

Large dielectric polarisation

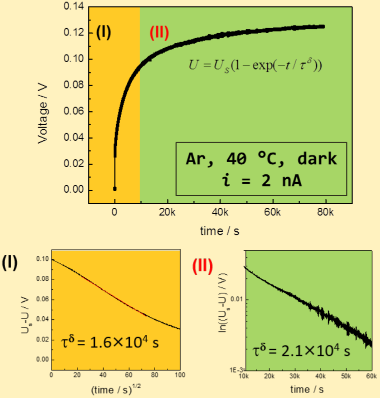


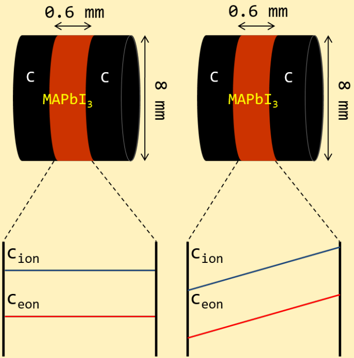
Juarez-Perez, *J. Phys. Chem. Lett.*, 2014

Outline

1. Evidences of ionic transport in $CH_3NH_3PbI_3$:
   - DC-galvanostatic polarisation
   - EMF measurements
2. Identification of the mobile defects:
   - Conductivity as f(exchangeable components)
   - Chemical modifications (doping)
3. Concluding remarks

Stoichiometric polarisation of $CH_3NH_3PbI_3$





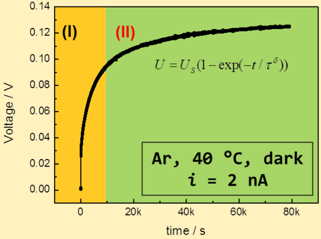
Without Bias	With Bias

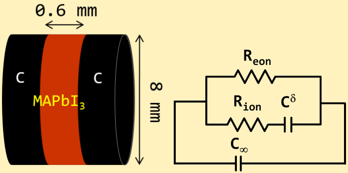
Yang *et al.*, *Angew. Chemie Int. Ed.* 2015

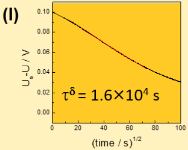
Extracted values:

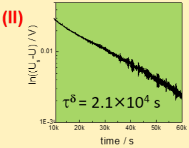
- $\sigma_{\text{ion}} = 7.7 \cdot 10^{-9}\ \text{S} \cdot \text{cm}^{-1}$
- $\sigma_{\text{eon}} = 1.9 \cdot 10^{-9}\ \text{S} \cdot \text{cm}^{-1}$
- $\text{D}^{\delta} = 2.4 \cdot 10^{-8}\ \text{cm}^2 \cdot \text{s}^{-1}$

Stoichiometric polarisation of $CH_3NH_3PbI_3$









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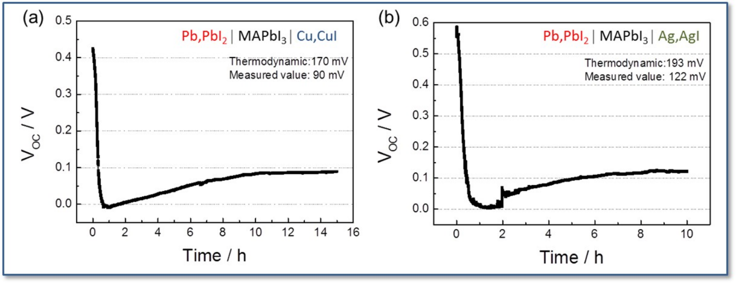
- $D^{\delta} = 2.4 \cdot 10^{-8}\ cm^2 \cdot s^{-1}$

$CH_3NH_3PbI_3$ is a mixed conductor with $\sigma_{ion} > \sigma_{eon}$ in dark conditions.

Since $\mu_{ion} << \mu_{eon}$, we expect ionic defects dominating.

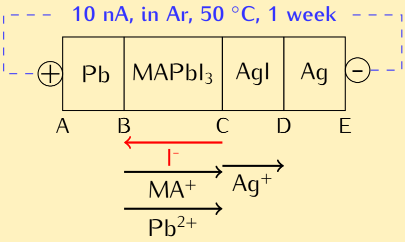
EMF measurements

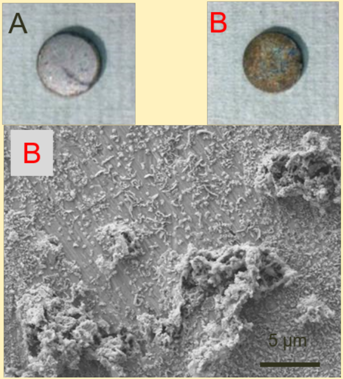


$$V_{OC} = t_{ion} \frac{\Delta_f G_{(PbI_2)} - 2\Delta_f G_{(CuI/AgI)}}{2F}$$

- EMF experiments show a clear ionic contribution.
- t_{ion} values in agreement with DC-galvanostatic data.

Identification of the moving ion





Further characterisations:

EDS and XRD confirmed the presence of PbI_2 on the interface B.

Yang *et al.*, *Angew. Chemie Int. Ed.* **2015**

We can conclude that:

Iodine is the moving ion in $CH_3NH_3PbI_3$.

Defect chemistry reactions:

1) $\frac{1}{2}I_2 + V_I^{\bullet} \rightleftharpoons I_I^{x} + h^{\bullet}$ $\quad K_1 = \frac{[h^{\bullet}]}{[V_I^{\bullet}]P_{I_2}^{1/2}}$

2) $\frac{1}{2}I_2 + MA_{MA}^{x} \rightleftharpoons V'_{MA} + h^{\bullet} + MAI$ $\quad K_2 = \frac{[V'_{MA}][h^{\bullet}]}{P_{I_2}^{1/2}}$

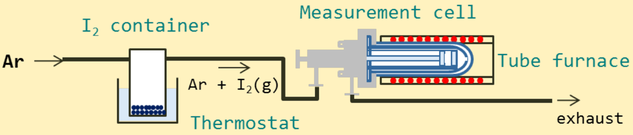
3) $MAI \rightleftharpoons V_I^{\bullet} + V'_{MA}$ $\quad K_S = [V'_{MA}][V_I^{\bullet}]$

4) $0 \rightleftharpoons h^{\bullet} + e'$ $\quad K_I = [e'][h^{\bullet}]$

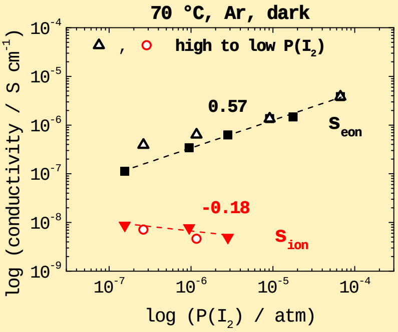
Assumptions:

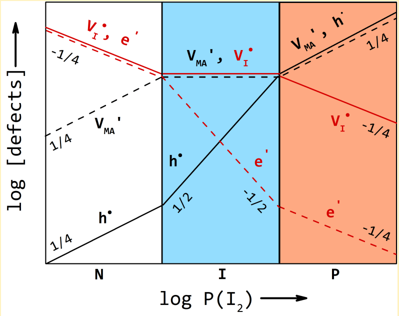
- Vacancies are more easily formed[1–2]
- No Pb defects (high ΔH_f and E_A)[3–4]
- I'_i found in literature with low E_A[5]

[1] Walsh *et al.*, *Angew. Chemie Int. Ed.*, **2015**, 54, 1791.
[2] Kim *et al.*, *J. Phys. Chem. Lett.*, **2015**, 5, 1312.
[3] Eames *et al.*, *Nat. Commun.*, **2015**, 6, 7497.
[4] Azpiroz *et al.*, *Energy Environ. Sci.*, **2015**, 8, 2118.
[5] Haruyama *et al.*, *J. Am. Chem. Soc.*, **2015**, 137, 10048.



Pure $CH_3NH_3PbI_3$: I_2 partial pressure

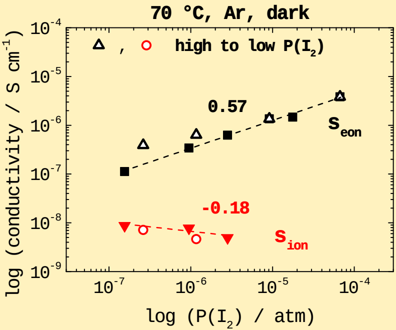


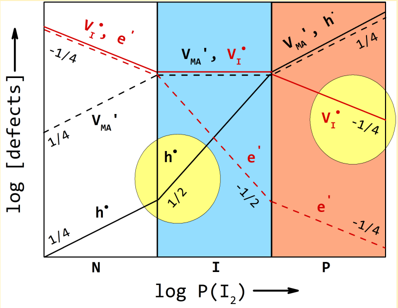


Pure MAPI $P(I_2)$:

- Semi-quantitative agreement
- σ_{eon} is p-type
- $V_I^{\bullet}$ is the mobile defect.

Pure $CH_3NH_3PbI_3$: I_2 partial pressure





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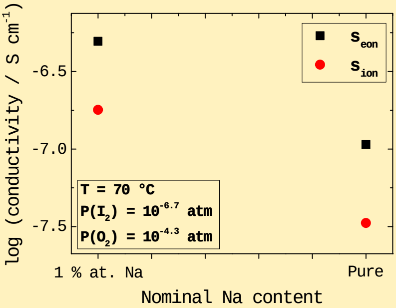
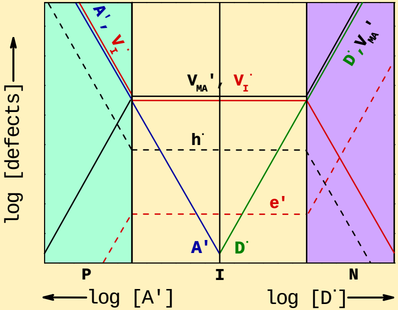
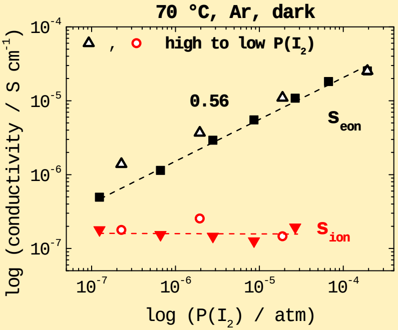
Na-doped $CH_3NH_3PbI_3$

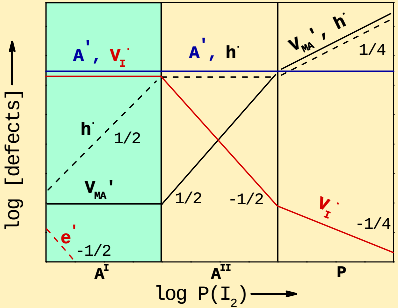




- Na'_{Pb} compensated by $\mathbf{V_I^\bullet}$ and $\mathbf{h^\bullet}$
- σ_{eon} and σ_{ion} increase with doping
- **Doping concentration is only nominal!**

Na-doped $CH_3NH_3PbI_3$: $P(I_2)$

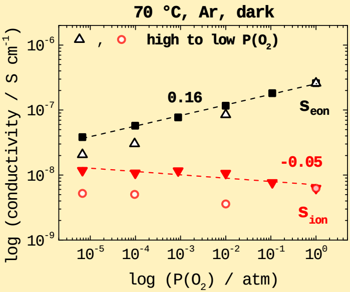


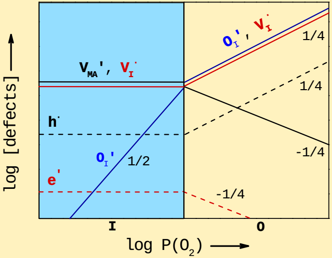


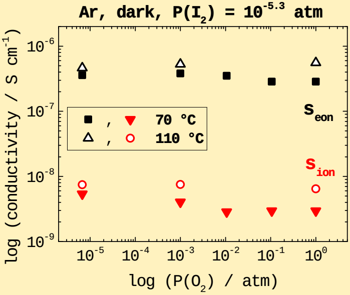
$CH_3NH_3Na_{0.01}Pb_{0.99}I_{2.99}$:

- No decrease in σ_{ion}
- Significant increase in σ_{eon}
- $V_I^{\bullet}$ is the mobile defect.

Pure $CH_3NH_3PbI_3$: O_2 partial pressure



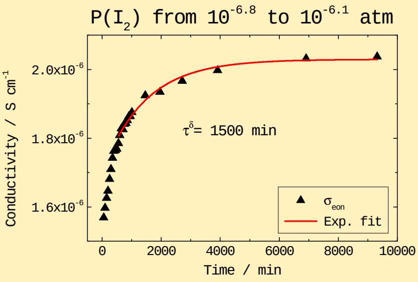




Pure $MAPbI_3$ $P(O_2)$:

- O_2 effect only in absence of I_2.
- O_2 can change I_2 activity over sample (surface reaction).

Conductivity equilibration: I_2 and O_2



- O_2 exposure has fast equilibration.
- I_2 equilibration is $\sim$ 40x slower.
- **Surface nature of O_2 interaction.**

Concluding remarks:

1. $CH_3NH_3PbI_3$ is p-type electronic conductor.
2. I^- is the mobile ion and $V_I^\bullet$ are mobile defects.
3. O_2 appears to only affect I_2 activity.
4. Electrical properties can be significantly tuned.

Effect of I_2, O_2 treatments under light has yet to be investigated.

Thank you for your kind attention!

Acknowledgments:
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