

## Quantitative evaluation of dark ionic transport in hybrid lead iodide perovskite ( $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ ) thin films and its implication on current-voltage hysteresis

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Organic-inorganic metal halide perovskites have rapidly emerged as a new class of materials with remarkable optoelectronic properties, notably as solar cells with power conversion efficiency reaching 23% under AM1.5 conditions.

The physics of such complex materials is far from being understood: for instance inconsistencies have been observed such as high carrier lifetime versus low mobility and low temperature preparation versus low defect density. So hybrid perovskites, for which a stoichiometric deficiency of one constituent may play a leading role (Schottky ionic disorder), do not behave like conventional semiconductors. Moreover photocurrent density-voltage hysteresis and poor stability is the main issue to be solved for commercial applications.

One possible interpretation for the observed hysteresis concerns the mixed conductivity for which the extraction of the ionic conductivity from the electronic one presents some difficulties. In this work, we synthesized solution-processed  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  polycrystalline films with an average crystal size of 0.4  $\mu\text{m}$ . We performed two independent measurements, **conductivity measurements versus temperature under dark conditions using transmission line method (TLM)** and **glow discharge optical emission spectrometry (GD-OES)**, a spectrochemical technique allowing direct determination of major and trace elements, **under electric bias conditions at room temperature**. From GD-OES we observed **directly** a migration of halide I ions under 1.5 V bias and determined a minimum value of iodide diffusion coefficient of order  $10^{-12}$   $\text{cm}^2/\text{s}$ . By plotting  $\ln(\sigma.T)$  versus  $1000/T$  at high temperature ( $T > 300$  K), where the conduction is dominated by the ions [1], we deduced independently a diffusion coefficient of the same order. An activation energy of 0.25 eV is also determined, corresponding to the activation barrier of vacancy migration for iodides, similar to what has been measured in small grain (0.3  $\mu\text{m}$ )  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films [2]. This value is comparable to that measured for the inorganic lead halide perovskites (0.29 eV), considered as ion-conducting materials since three decades [3] and is in agreement with the calculated activation energy of anionic vacancy migration (0.32 eV) deduced from first-principles density functional theory calculations [4,5]. Moreover from the conductivity data at low temperature (260 K), it is found that electronic conductivity emerges with a low electron mobility ( $3 \times 10^{-2}$   $\text{cm}^2/\text{V.s}$ ), ascribed to the polycrystalline perovskite films.

Due to the slow dynamics of the anion migration at room temperature (some seconds), it is shown that the electron and hole concentrations are sensitive to the electrochemical potential, what explains the density-voltage hysteresis observed under dark conditions in the  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  polycrystalline films as a function of time and temperature.

[1] T.Y. Yang et al., *Angew. Chem.* 54, 7905 (2015).

[2] J. Xing et al., *Phys. Chem. Chem. Phys.* 18, 30484 (2016).

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[4] J. Haruyama et al., *J. Am. Chem. Soc.* 137, 10048 (2015).

[5] C. Eames et al., *Nat. Commun.* 6, 7497 (2015).