# Quantification of Point Defect Energy in $MDACl_2$-stabilized Perovskite Solar Cells


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## Abstract

Perovskite solar cell efficiency is reduced by Shockley-Read-Hall (SRH) recombination, in which charge carrier collection is diminished by the presence of sub-band gap energy states, called traps. Theoretical studies have credited some crystallographic point defects with the production of such states.[1] By understanding how these defects form and contribute to a material's electronic structure, we will gain insight into routes of SRH recombination and the related loss of efficiency. Thus, we aim to measure and describe the nature of formation of traps in real materials. External quantum efficiency measurements are used to extract a Gaussian distribution of trap states.[1] Capacitance techniques enjoy enhanced sensitivity to traps in the absorber layer, however, are accompanied by complications associated with the hysteretic perovskite system.[2] Methylenediammonium dichloride-stabilized alpha-formamidinium lead triiodide perovskite contain interstitially incorporated chloride ions and have impressive power conversion efficiencies of 23.7%,[3] leading to their use in this study. EQE spectra of $MDACl_2$-stabilized samples gave a small defect signal with transition energy of 1.08 ± 0.01 eV. Findings may point to material suppression of sub-gap defects associated with $MDACl_2$–stabilization compared to alternative compositions.


## Methods

**Current-Voltage (I-V) Curves:[4]**

A Keithley 2400 source meter was used to measure I-V curves produced under 1-sun illumination with a model 94083A Oriel Sol3A solar simulator.

**External Quantum Efficiency (EQE):[5]**

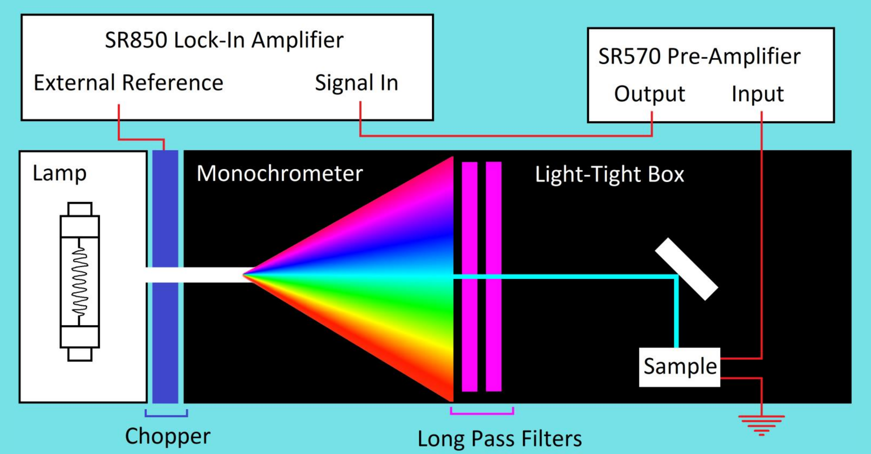



**Figure 1:** EQE Experimental Schematic. Light from a 550 W quartz-tungsten-halogen lamp is passed through a 0.5 focal length, f/4.5 monochromator with 1 of 4 diffraction gratings and is chopped at 1 kHz. Long pass filters eliminate stray light. The photocurrent is sent through the SR570 current-voltage amplifier and is measured by the SR850.

**EQE Analysis:[5]**

$$EQE\ Signal = \frac{Electron\text{–}Hole\ Pairs\ Collected}{Number\ of\ Photons\ Incident} = \frac{Collected\ Current * Incident\ Energy}{Incident\ Flux * Area\ of\ Illumination} \quad (1)$$

$$Incident\ Flux = \frac{Collected\ Reference\ Diode\ Current}{Diode\ Responsivity * Area\ of\ Illumination} \quad (2)$$

**EQE Signal Fitting:[5]**

$$\alpha = \alpha_0 \exp\left(\frac{E-E_g}{E_U}\right) + \sum_i Ai\left[1 + \mathrm{erf}\left(\frac{E-E_{d,i}}{\sigma_{d,i}\sqrt{2}}\right)\right] \quad (3)$$

**Capacitance-Voltage (C-V) Measurements:[6]**

Measurements are made in the dark with an AC perturbation of 30 mV at 10 kHz. AC and DC signals produced by the SR850 are combined in an adder box, sent through the sample to the SR570, and back to the SR850 for measurement of capacitance and voltage. Voltage-modulation of the depletion layer width should allow the extraction of the absorber dopant plus defect density (N) and built-in potential ($V_{bi}$) using Mott-Schottky analysis and C-V profiling, demonstrated in equations 4 and 5, respectively.

$$C^{-2}(V) = \frac{2(V_{bi}-V)}{q\epsilon N} \quad (4)$$

$$N(x) = \frac{2}{q\epsilon}\left(\frac{\partial C^{-2}}{\partial V}\right)^{-1} \quad (5)$$

## Results

**Figure 2: I-V Curves of $MDACl_2$-stabilized $\alpha$-$FAPbI_3$.** Cell efficiency is taken as the maximum power point of the I-V curve over the power of incident light. Sample 2 appears to have a higher efficiency than sample 1. Over time, sample 1 efficiency diminished. Hysteresis is present in both samples.

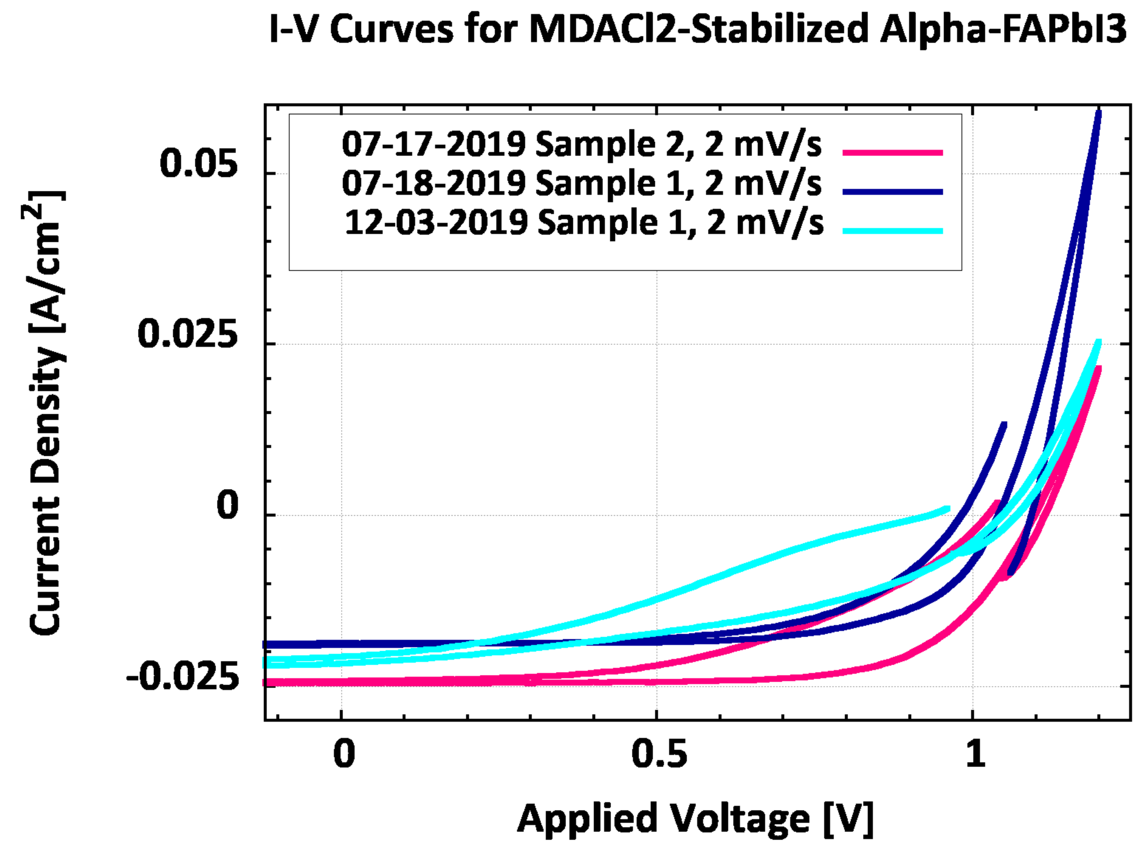



**Figure 3: EQE Spectra Comparison.** Sample 1 appears to exhibit a defect signal, while sample 2 does not. Sample 1 was thus fit. The defect signal was fit with equation 3. The defect transition energy of sample 1 was calculated at 1.08 ± 0.01 eV. Samples of $MAPbI_3$ and $FAPbI_3$ are plotted for comparison. Both appear to have a larger defect magnitude over a wider voltage range than sample 1. Note, the bandgaps of the $MDACl_2$-stabilized $\alpha$-$FAPbI_3$, $MAPbI_3$, and $FAPbI_3$ samples are different.

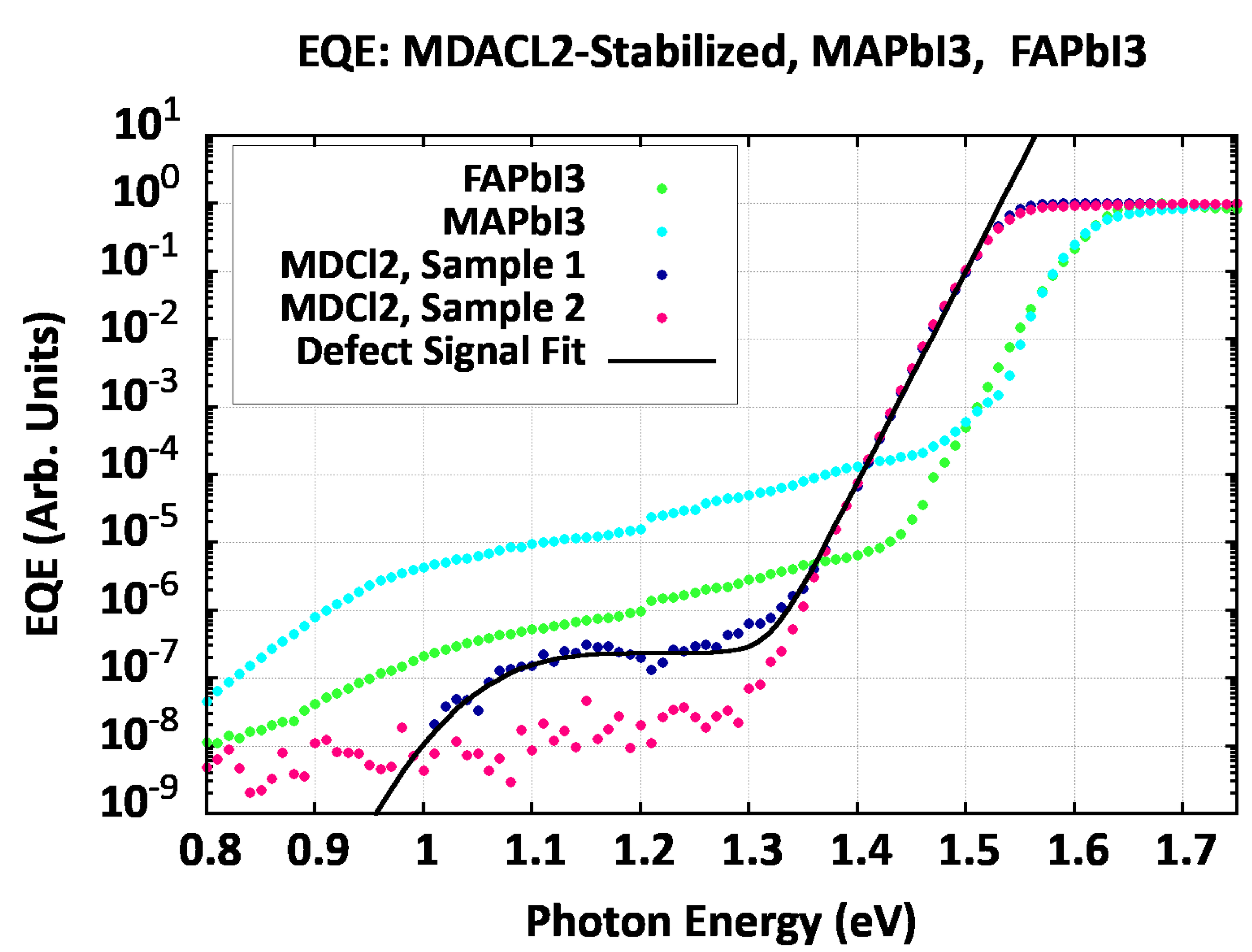
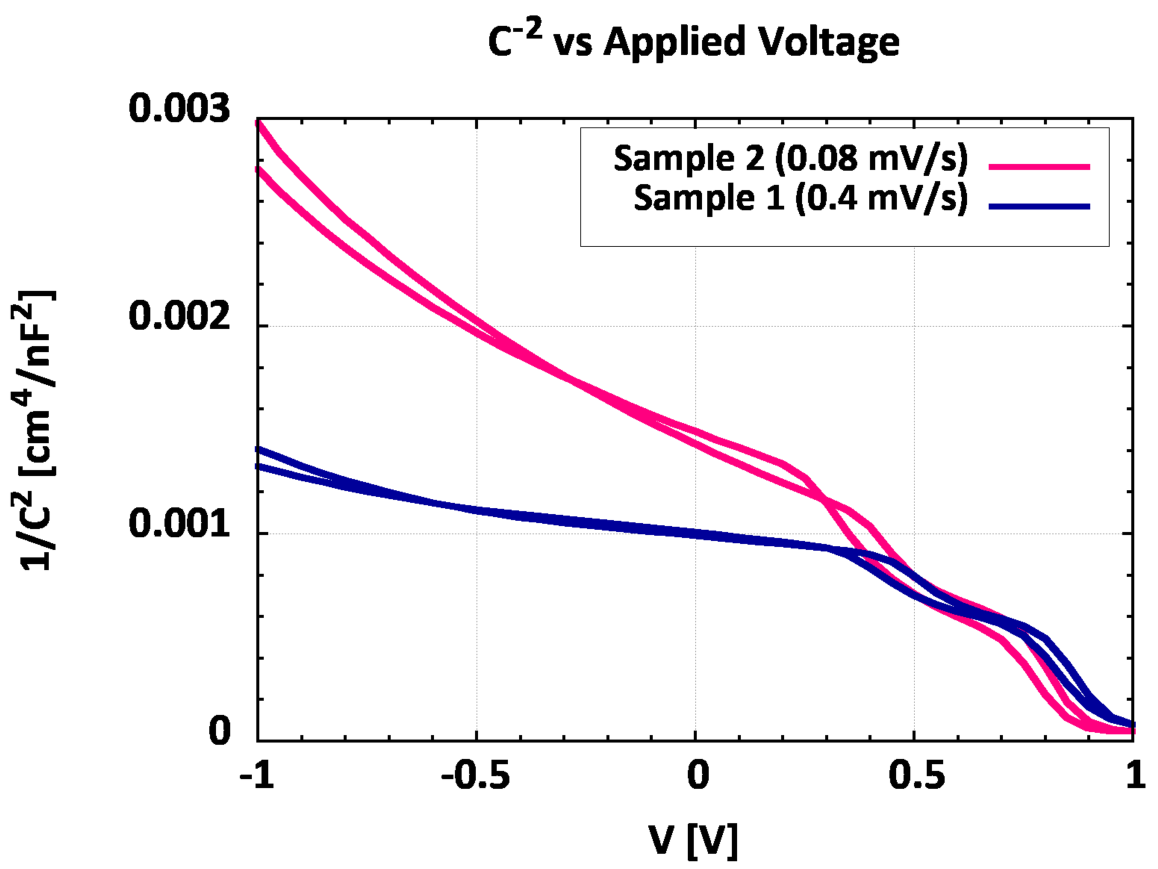



**Figure 4: Mott-Schottky Plot ($C^{-2}$ vs. V) of $MDACl_2$-stabilized $\alpha$-$FAPbI_3$** The difference in slopes between samples 1 and 2 demonstrates a larger defect density is present in sample 1, assuming samples 1 and 2 have the same dopant density. This is consistent with EQE spectra of Figure 3. Hysteresis is present in both data sets. Equation 4 assumes a flat N near the interface,[6] however, this does not appear to be the case given the non-constant slope. The built-in potential appears larger than realistically expected. This may imply the samples have graded junctions or another capacitance is contributing, potentially that of hysteretic capacitance.




## Research Questions

**How do point defects contribute to the electronic structure of $MDACl_2$-stabilized $\alpha$-$FAPbI_3$ perovskite solar cells?**
**What is the defect energy and related density of sub-gap states?**
**What types of defects are these and where are they physically?**

## Conclusions

EQE spectra in Figure 3 displays a defect with transition energy of 1.08 ± 0.01 eV, found in sample 1 of $MDACl_2$-stabilized $\alpha$-$FAPbI_3$ perovskite. The defect shows a lower density of states than the $FAPbI_3$ and $MAPbI_3$ samples. This suggests $MDACl_2$ –stabilization may suppress sub-gap defects with greater efficacy than alternative compositions. It would be interesting to study multiple stabilizing agents of varying compositions in order to confirm this suggestion, but also to better understand how composition affects defect states in general.

Capacitance methods may better answer the above outlined research questions. However, this will be difficult with the additional consideration that the simplest capacitance method, C-V measurements, do not follow traditional theory. This divergence from theory should be further explored before moving on to more advance capacitance techniques. Transient photocapacitance (TPC) is one such method and it can be used to extract information about defect energies, similar to EQE, however, with an enhanced sensitivity to the absorber layer.[2] Drive level capacitance profiling (DLCP) is another technique capable of differentiating between the dopant and defect densities.[7] However, if hysteresis is contributing to capacitance, such methods may require much more consideration when being used to provide defect data on perovskite solar cells. Though, in the event that C-V results are pointing to the presence of a graded junction, TPC may still yield significant results. Either way, the experimental divergence from theory in C-V measurements should be investigated further to help understand how hysteresis may affect more advanced capacitance techniques before they're used to answer the outlined research questions.

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