Supporting Information

Optoelectronic Properties of $(CH_3NH_3)_3Sb_2I_9$ Thin Films for Photovoltaic Applications

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Photo thermal deflection spectroscopy (PDS)

Photo thermal deflection spectroscopy (PDS) is a sensitive technique to measure the optical absorption characteristics of thin films by the change of the refractive index due to heating of a medium by pump light. A full theoretical description of the PDS measurements is given by W. B. Jackson et. al.[1-2]. PDS was measured in transverse mode. In the given set up, a 100 W halogen lamp (HLX64625 Xenophot) was used as pump beam light source. The halogen lamp was used together with different filter (RG715, OG590, GG435+KG3, BG39, Si, Ge) and a JOBIN YVON grating monochromator "240M". PDS was measured in the range of 0.5 – 3.0 eV with a step size of 20 meV. As probe beam a diode laser (650 nm) is used. The heating/temperature of the sample is measured with a pyrometer. The deflection of the laser probe beam is measured with a quadrant diode. The sample is measured in a cuvette with FC75 solution as optical medium which does not react with the $(CH_3NH_3)_3Sb_2I_9$ perovskite. By this also possible degradation of $(CH_3NH_3)_3Sb_2I_9$ due to air and moisture is prevented during the measurement.

Photoluminescence measurement (PL)

For the room temperature photoluminescence spectroscopy (PL) the $(CH_3NH_3)_3Bi_2I_9$ perovskite samples were measured in a nitrogen filled sample box with quartz glass windows. For excitation a sapphire laser (coherent Inc.) with a wavelength of 488 nm and a focused spot size of < 1 μm is used. The luminescence spectra are detected via a Horiba iHR320 spectrometer with an Andor Si CCD camera (iDus Series).

J-V measurement

J-V curves were measured with a LED set up directly after deposition of the metal contacts inside a nitrogen filled glovebox. The light intensity of the LED was calibrated to known short circuit current from *EQE* measurements. A Keithley 2400 SMU was used to record the *J-V* data. The curve was measured from -0.2 V to 1.0 V with a step size of 0.01 V and a DC delay time of 0.15 s. The dark current voltage curve was measured over a range from -0.2 V to 1.2 V averaged over 3 measurements for each point.

EQE measurement

A Xenon lamp XBO150W is used as light source with OWIS 5 position filter wheel. A grating monochromator Bentham TMC300 is used. To measure the current of the sample a femto current voltage converter and a HMS Lock-In amplifier are used together with a femto Lock-In amplifier as monitor detector.

$(CH_3NH_3)_3Sb_2I_9$ thin film fabrication

The $(CH_3NH_3)_3Sb_2I_9$ thin films were prepared by spin-coating a precursor solution. The precursor solution is prepared by solving SbI_3 (Alfa Aesar 99.999%) and MAI (Dyenamo) with a molar ratio of 2:3 in a mixture of GBL:DMSO. The overall concentration was 35 wt%. We tried out two different spin-coating procedures. For the 1 step process the precursor solution was spincoated at 3000 rpm for 45 s. In the 2 step process the precursor was spin coated at 3000 rpm for 10s going up to 5000 rpm 20s. During the second spin coating step toluene was dropped on top of the sample to achieve a smooth surface. For the optical characterization the Sb-perovskite was fabricated on quartz glass substrates and for device fabrication on ITO/PEDOT substrates.

$(A)_3Bi_2I_9$ thin film fabrication

The $(A)_3Bi_2I_9$ thin films (A= CH_3NH_3, $(CH(NH_2)_2)_3$, Cs) were prepared by spin-coating a precursor solution. The precursor solution is prepared by solving BiI_3 (Alfa Aesar 99.999%) and MAI (Dyenamo), FAI (Dyesole) or CsI (Sigma-Aldrich) with a molar ratio of 2:3 in a mixture of GBL:DMSO with an overall concentration of 35 wt%. Just like for the Sb-based devices, we prepared samples using the two-step process with the toluene drop. Spin coating parameters were chosen identical to the preparation of the Sb-based perovskites that were also deposited on ITO/PEDOT substrates for optical measurements.

Device fabrication

Structured ITO substrates were bought from Psiotec. The substrates were cleaned with soap (Helmax III), Aceton and Isopropanol. After this the substrates were treated with an oxygen plasma using a Diener Zepto plasma cleaner. The PEDOT:PSS (Ossila M121 Al4083) was spin-coated in air at 5000 rpm for 60s and annealed in N_2 at 110°C 10 min. The Sb-perovskite layer was applied as described above. As electron transport layer a 2wt% solution of $PC_{61}BM$ (Solarmer) in Chlorobenzene was spin-coated at 1000 rpm 60 s. As interlayer a ZnO nanoparticle ink (Nanograde Ltd. N10) was used and spin coated at 3000 rpm 60 s. Finally the Aluminium contact (150 nm) was evaporated on top of the layer stack. The active area of the solar cell was between $0.06mm^2$ and $0.16\ mm^2$.

Simulation of J_{sc} vs. thickness

The simulations used for Figure 3b were done with the software ASA (TU Delft, http://www.ewi.tudelft.nl/en/the-faculty/departments/electrical-sustainable-energy/photovoltaic-materials-and-devices/software-platform/asa-software/) using optical data measured for the active layers and the contact layers. ASA uses a transfer matrix model to calculate the optical generation rate at every position in the active layer. In addition to the optical simulation an electrical simulation was performed using values for mobility and recombination coefficient that were sufficiently high (for the mobility) and low (for the recombination coefficient) to ensure that there were no recombination losses at short circuit.

Figures:

Figure S1 shows the difference of the XRD pattern for the crystalline $(CH_3NH_3)_3Bi_2I_9$ thin film and the amorphous layer after the toluene drop.

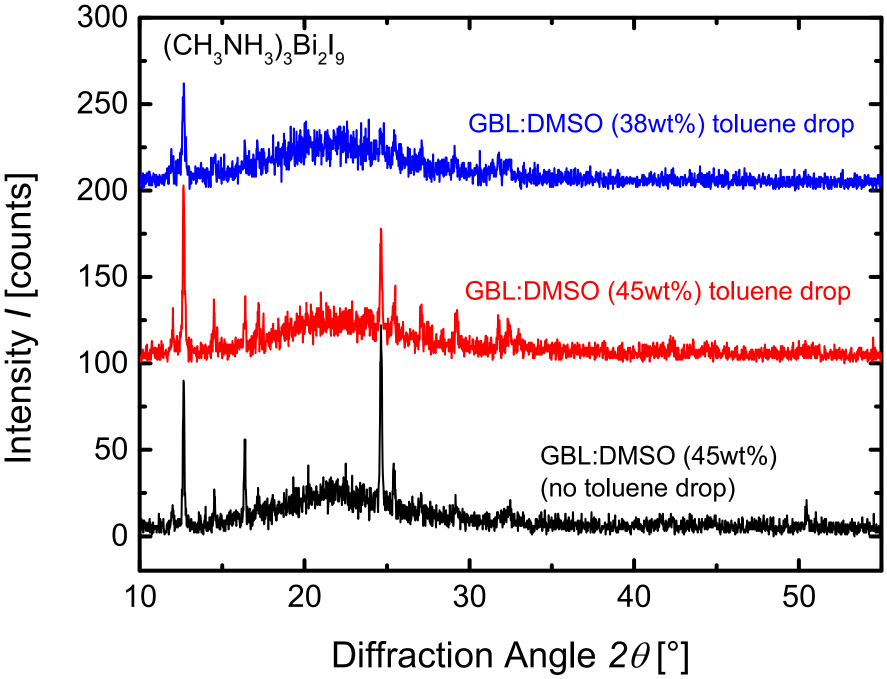

Figure S1. Comparison of XRD pattern of an $(CH_3NH_3)_3Bi_2I_9$ sample from 1 step process (black) and two amorphous/low crystallinity sample after toluene drop. Note that the samples for absorption coefficient measurements were prepared with 35 wt% and toluene drop but XRD measurements were only done for samples with slightly higher concentration shown here.

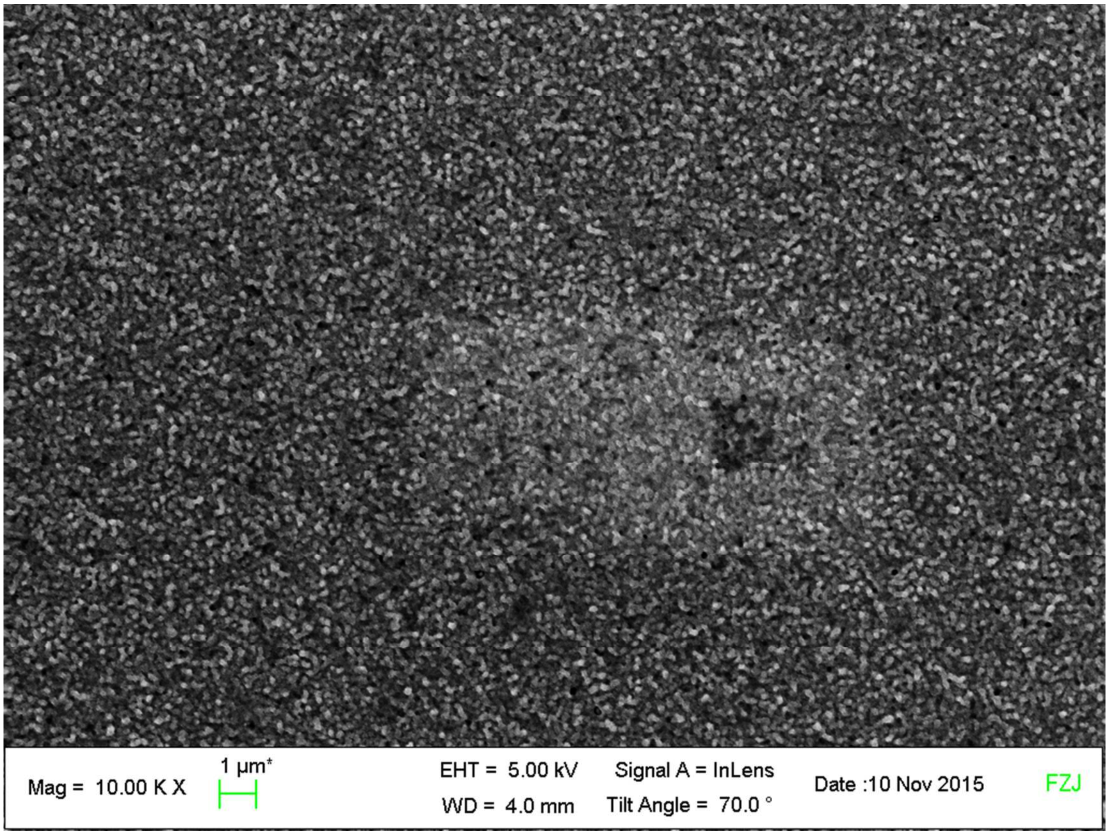

Figure S2: SEM image of a $(CH_3NH_3)_3Bi_2I_9$ sample after the toluene drop showing no large crystallites as was the case for the Sb-based films

To determine the band gap of $(CH_3NH_3)_3Sb_2I_9$ a direct band gap was assumed and the value for the band gap energy was calculated using a Tauc plot which is shown in **Figure S3.**

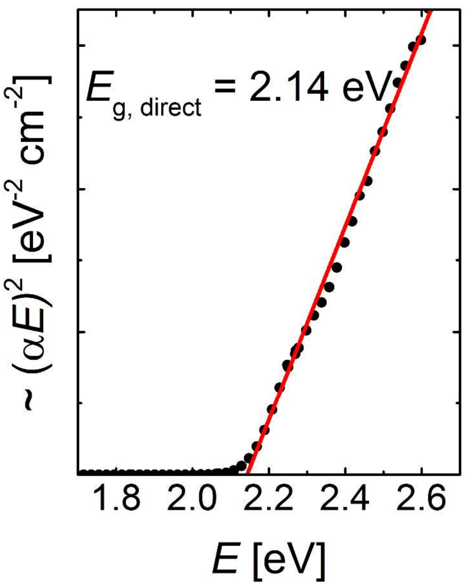

Figure S3. Tauc plot of absorption spectrum of $(CH_3NH_3)_3Sb_2I_9$ with linear fit to determine the direct optical band gap.

The different Urbach tail energies for the Bi-perovskite compound where calculated by fitting an exponential of the form $\exp(E/E_u)$ to the exponential part of the absorption onset measured with PDS. **Figure S4** shows the different plots with the relevant fits.

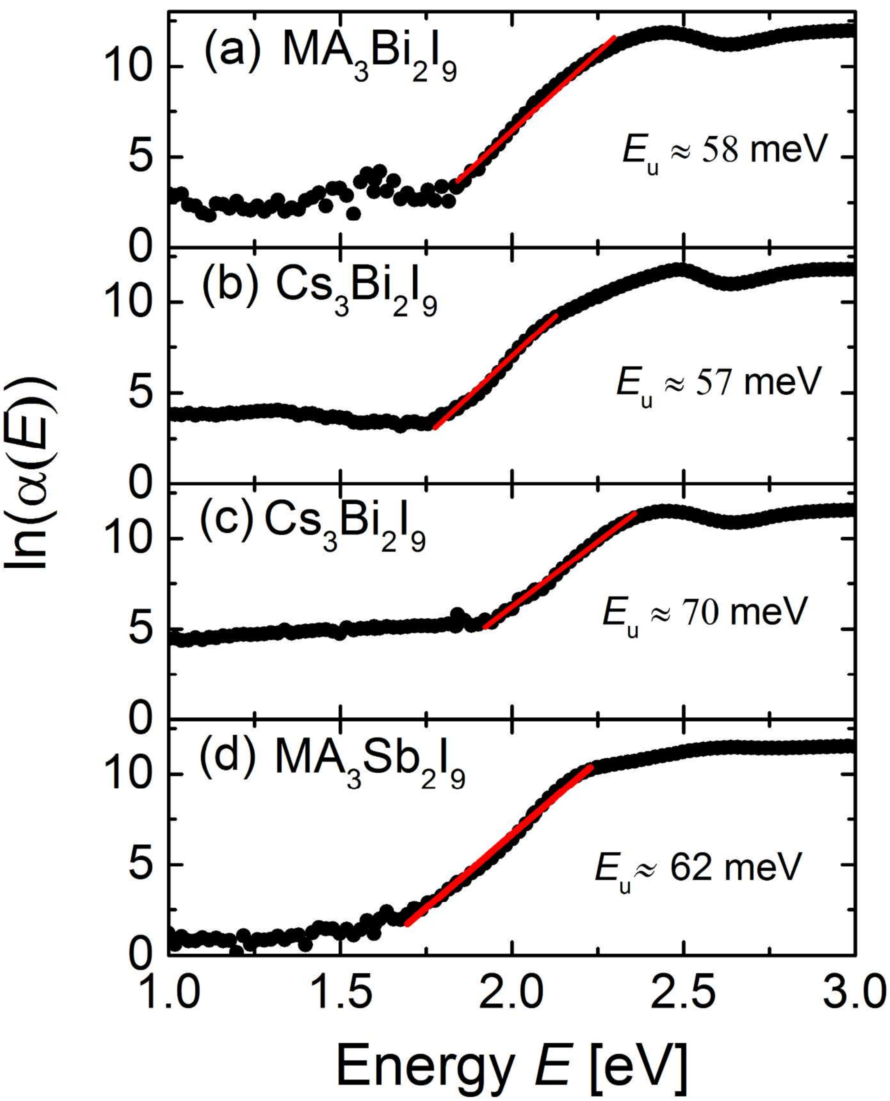

Figure S4. PDS measurement of the different Bi-perovskite compounds and the Sb-perovskite with fit function from the form exp(E/E_u) to determine the Urbach tail energies.

In **Figure S5** the dark *J-V* curve of the Sb-perovskite is shown.

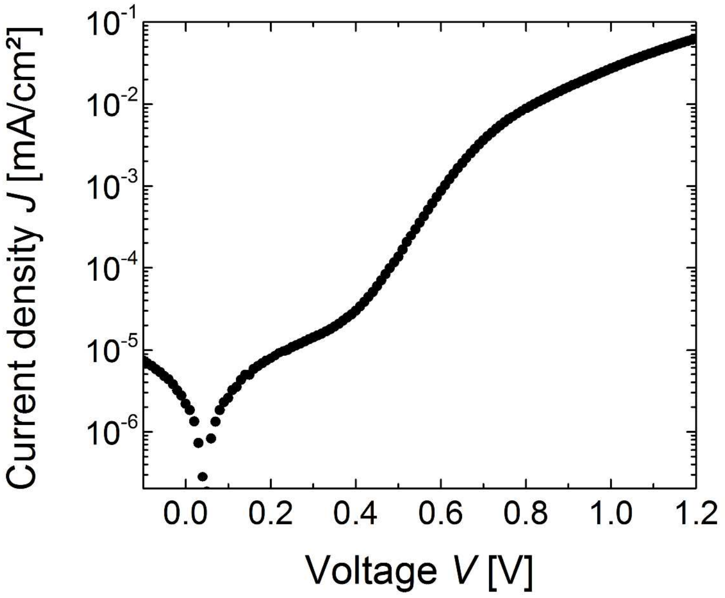

Figure S5: Dark *J-V* curve of $(CH_3NH_3)_3Sb_2I_9$ solar cell.

1. Boccara, A. C.; Jackson, W.; Amer, N. M.; Fournier, D., Sensitive photothermal deflection technique for measuring absorption in optically thin media. *Opt. Lett.* **1980,** *5* (9), 377-379.

2. Jackson, W. B.; Amer, N. M.; Boccara, A. C.; Fournier, D., Photothermal deflection spectroscopy and detection. *Appl. Opt.* **1981,** *20* (8), 1333-1344.