Photo-Seebeck Effect in Methylammonium Lead Iodide Thin Films

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Abstract

In recent years, the world has seen an increased dependence on renewable sources of energy. Among these, solar energy presents a growing field with many potential areas of research, including development of a viable active region in solar cells where light can be converted to electricity. Perhaps the most captivating emerging group of materials is the family of perovskites with structure ABX_3, where A and B are cations and X is an anion. One potentially viable and efficient perovskite is methylammonium lead iodide ($CH_3NH_3PbI_3$) or $MAPbI_3$. While $MAPbI_3$ is of great interest to researchers, some of its most fundamental transport properties have yet to be thoroughly studied. In this research, we measure the Seebeck coefficient of thin films of $MAPbI_3$ as a function of conductivity for various light intensities and wavelengths. Seebeck data is very difficult to obtain without photoexcitation, and we utilize narrow-band high-power light emitting diode (LED) light sources spanning blue to infrared to populate the electronic conduction and valence bands. Our results are in rough agreement with accepted Boltzmann transport theory, and our modeling will help elucidate relationships between the concentration of free charge carriers, and their effective masses and scattering mechanisms.

Background

Methylammonium Lead Iodide ($MAPbI_3$)

- High efficiency[1] (~22%) perovskite (ABX_3) solar cell material
- Efficiencies have been increasing and have exceeded traditional solar cell materials (i.e. Silicon)
- Material remains understudied – particularly more detailed transport properties (charge carrier density, effective mass, & scattering mechanisms)

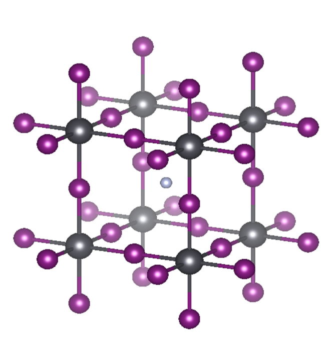

Figure 1: Atomic structure of $MAPbI_3$

Figure 2: $MAPbI_3$ thin film

Seebeck Effect

- Temperature difference across a sample results in an induced voltage
- Voltage depends on temperature gradient according to the Seebeck Coefficient, S, where

$$S = \frac{\Delta V}{\Delta T}$$

- Provides a more detailed understanding of electrical transport properties (effective mass, scattering mechanisms)

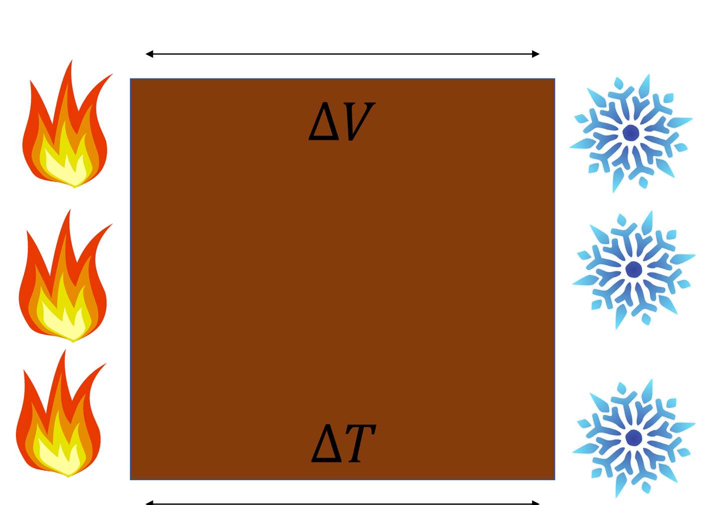

Figure 3: Illustration of Seebeck Effect

Seebeck Coefficient & Conductivity

- Boltzmann transport theory for parabolic bands gives equation[2]

$$S = C\frac{k_B T}{e}\frac{1}{E_F}$$

where C: dimensionless positive constant
k_B: Boltzmann's Constant
T: Temperature in K
e: electronic charge
E_F: Fermi Energy

- We assume that:
  - ✓ *Mobility of holes is much greater than mobility of electrons*
  - ✓ *Mobility of holes is insensitive to light illumination (independent of conductivity)*
- We can then conclude the following relationship between S and conductivity, σ

$$E_F \propto n^{2/3} \rightarrow S \propto n^{-2/3} \rightarrow S \propto \sigma^{-2/3}$$

Experiment

- Films are prepared via spin coating process at Case Western Reserve University and kept under inert atmosphere. Thickness ~ 250 nm
- 60 nm-thick Au/Pd electrodes pads are are sputter-coated for electrical contact to the sample. Fine wires are affixed to the electrodes with Ag paste.

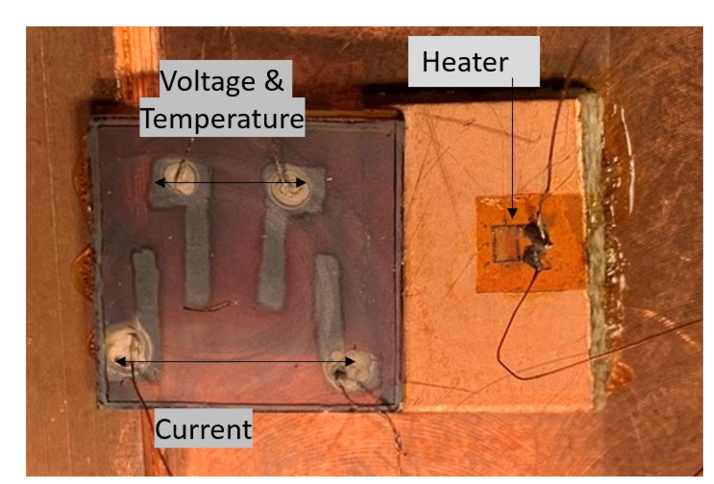

Figure 4: Image of film after sputter-coating and wiring

- Film is excited by 3 different colors of LED: red (660nm), green (565nm), blue (455nm) in an Ar gas-filled chamber during conductivity and Seebeck measurements
- Thermocouple voltages measured by Keithley 2182 nanovolt meters, sample voltage measured with Keithley 614 Electrometer, and heater/sample current applied with Keithley 2400 Sourcemeter

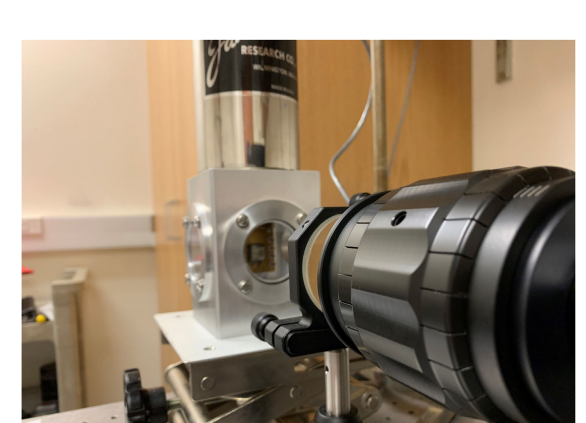

Figure 5: Image showing light path of LED and inside of cryostat with mounted film

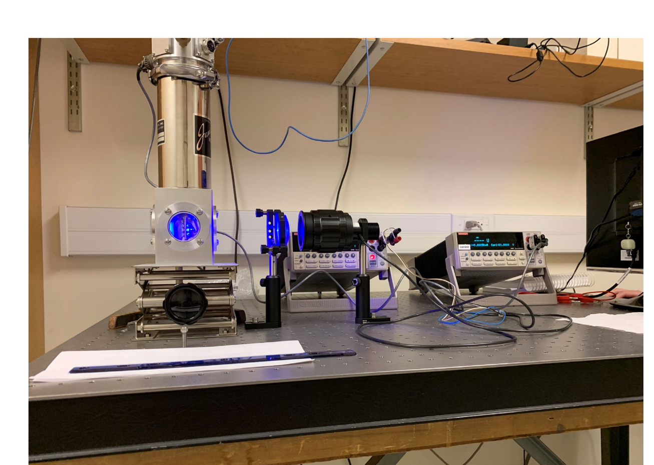

Figure 6: Image of full experimental setup with blue LED and meters for measuring current and voltage, computer to operate LabVIEW

Results

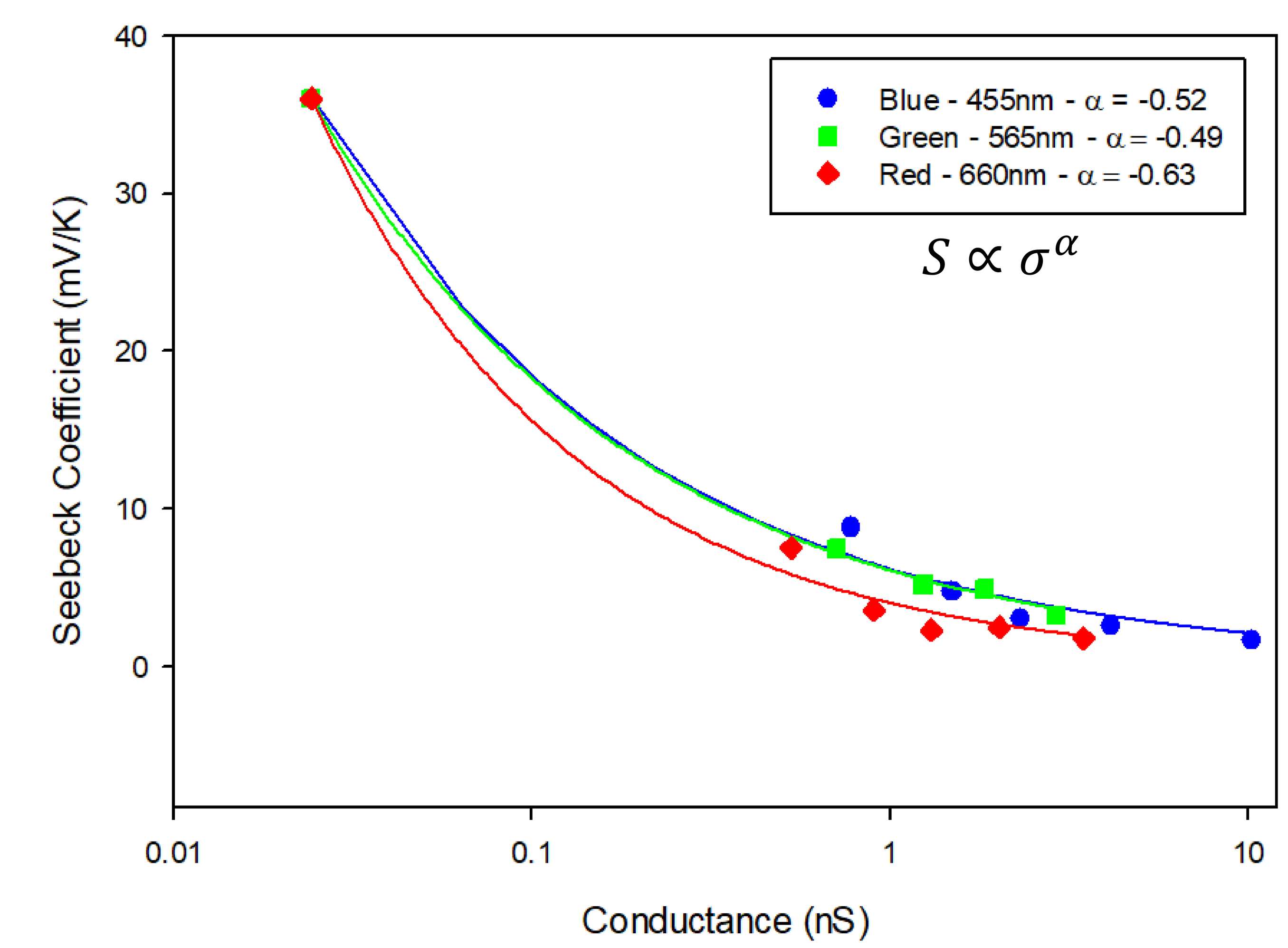

Figure 7: Plot of Seebeck Coefficient vs conductance with power law exponents shown

Conclusions

- Photo-Seebeck for various excitation wavelengths is believed to be novel data
- Preliminary measurements suggest rough agreement with accepted transport theory
- Measurements are also in agreement with prior modeling and predictions
- Reliable Seebeck data can help further understanding of transport properties of $MAPbI_3$
- Positive Seebeck coefficients in light and dark imply holes are dominant charge carrier in both instances
- Apparent distinction between red and blue/green Seebeck coefficient, warrants further investigation
- Future measurements to encompass a wider range of conductivity values

References

[1]Green M. A.; Emery K.; Hishikawa Y.; Warta W.; Dunlop E. D.; Levi D. H.; Ho-Baillie A. W. Solar cell efficiency tables (version 49). Prog. Photovoltaics 2017, 25, 3.10.1002/pip.2855.

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