Carrier Mobility in Methylammonium Lead Iodide Perovskite Solar Cells: Mobility Versus Composition in Spin Coated and Vapor Deposited Samples

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Carrier Mobility in Methylammonium Lead Iodide Perovskite Solar Cells: Mobility Versus Composition in Spin Coated and Vapor Deposited Samples

Abstract
We performed research on a set methylammonium lead iodide (MaPI) perovskite solar cell samples, including samples produced both by vapor deposition and spin coating. We used time resolved THz spectroscopy to measure carrier mobility in the samples and excitation of vibrational modes in the THz and IR spectra to gauge relative sample compositions (ratio of PbI to Ma). Plotting carrier mobilities against composition ratios, we found a peaked distribution of carrier mobilities suggesting an ideal ratio of lead iodide to methylammonium to maximize mobility. We also observed that the spin coated samples had considerably less variance in their composition ratios compared to the vapor deposited samples, and were clustered close to the peak of the graph. However, while the vapor deposited samples displayed a much higher compositional variation, vapor deposited samples with compositions similar to the spin coated ones also had similarly high mobilities. This indicates that the vapor deposited samples aren't inherently bad, just have more variance in their compositions.

Keywords
perovskite, methylammonium, lead iodide, methylammonium lead iodide, THz spectroscopy, solar, terahertz

Cover Page Footnote
The Holmes research group at the University of Minnesota Rohan Lichtenberg

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I. Introduction

As climate change worsens in large part due to unsustainable energy sources like petroleum, it is increasingly vital to research and develop renewable energy infrastructure such as solar panels. Solar panels in use today are overwhelmingly made using silicon wafers, but another promising material in this field are lead halide perovskites.

Perovskites are another type of semiconductor, but the process for making solar cells out of them is quite a bit simpler than for silicon. In laboratory testing, perovskites samples have shown efficiencies of greater than 20%, which is on par with many silicon solar panels currently in use [1]. Further research and refinement of these materials will only improve their performance, and offer a valuable alternative material to silicon. More importantly though is that while silicon solar cells require a complicated and costly process for forming crystal lattices for wafers, perovskite solar cells can be made through comparatively much simpler methods of solution processing onto a substrate, either by spin coating or vapor deposition [2]. One significant drawback to perovskites is that unlike silicon solar cells, perovskites are highly sensitive to moisture and high energy light and degrade quickly under exposure to water vapor or ultraviolet light, meaning that in their current state they couldn’t be used for large scale, outdoor solar farms. This is an important and ongoing area of research in the field of perovskites, but outside the scope of this project. It is important to understand this drawback, but further comment on it will not be made.

Perovskites are commonly composed of two constituent materials, such as the samples tested in our research: methylammonium lead iodide (MaPI, chemical structure CH₃NH₃PbI₃), where the components are methylammonium and lead iodide. In spin coating, the two components are deposited onto a spinning substrate together in a one-step process, or one at a time in a two step
process [1]. Vapor deposition involves the coevaporation of the components onto the substrate, usually under vacuum conditions [1]. If the production of perovskite solar cells were to be developed to the point mass producibility like that of silicon cells, these simpler methods could potentially be much cheaper than those of silicon, and their widespread use could reduce the cost of generating solar energy overall, so further research into their performance is extremely important [1].

Our research was conducted in collaboration with the Holmes Research Group at the University of Minnesota, whose work centers around a novel method of perovskite vapor deposition at low temperatures. The Holmes group produced a set of MaPI samples, some that were made using vapor deposition and others made by spin coating, and our project was to characterize the samples by measuring their carrier mobility and relative composition (ratio of lead iodide to methylammonium), and look for how the mobility varied with sample compositions, as well as to compare the performance of the samples made using the two different processes. The composition of perovskite samples can have significant effects on how they perform in terms of their carrier mobilities, so working with the Holmes group our research was aiming to find a basic relationship between the two. For perovskites to see the same widespread use, and more importantly production, as silicon, they need to be able to be mass produced. A better understanding of how MaPI perovskites’ composition affects performance and how to maximize that performance is a crucial precursor to that mass production, since ideally they would be produced with the optimum composition ratios.

Our samples were produced in six smaller subgroups, labeled A through F, and had a band gap of roughly 1.5 eV – 1.55 eV. Groups A, B, C, and D were all made by vapor deposition, while E and F were made by spin coating. The samples within each group were made at the same time
using the same process, and so were theoretically identical to one another. These six groups were further broken into two-group pairs (A and B, C and D, E and F). Each pair were made with the same process and by the same person, but with the groups in each pair using different conducting layers, tin oxide (SnO$_2$) or PEDOT. Each pair of groups was made with the intent of isolating the variable of the different conducting layers to track a correlation between carrier mobility and conducting layer if one existed, given that the group pairs (ex. A and B) were otherwise the same. However, we ultimately did not find a relationship between carrier mobility and conducting layer, so the group labels were ultimately a tool for keeping track of individual samples.

II. Methodology

A. Relative Sample Composition

For our purposes, we simply wanted a general measurement of the ratio between the two MaPI components rather than the exact material compositions of each sample. To do this, we took advantage of vibrational modes in each of the two components that are visible when excited by different frequencies of radiation: N-H bond vibrational modes in methylammonium are visible under infrared (IR) frequency radiation and the Pb-I vibrational modes in lead iodide are visible under terahertz (THz) frequency radiation. We collected absorption data for each sample at IR and THz frequencies, using a measure of the strength of the absorption as a proxy for the proportion of the sample composed of the associated component. This process involved measuring the absorbance of our samples, as well as that of a blank substrate, and then subtracting the substrate data from that of the sample to isolate the absorption due specifically to the perovskite films.
We used an infrared spectrometer to measure the IR absorbance of our samples, and its associated data analysis program to generate a graph of the absorbance versus wavenumber. We identified the absorbance stretch associated with the N-H vibrational mode in each sample, and measured the area under that stretch to use as our stand-in for the proportion of methylammonium in the samples. For the THz absorbance, we used an XL-500 laser system using a zinc telluride crystal as a THz emitter, to measure the transmission through each sample versus frequency. In these graphs, we see two stretches of low transmission, which are the absorption lines associated with the Pb-I vibrational modes. We approximated the concentration of lead iodide in each sample by plotting a curve fit to the transmission data: the better the fit matched the data, the stronger the match between the curve fit and the data, the higher the concentration of lead iodide.

Finally, we divided our value for the lead iodide concentration by that of the methylammonium for each sample, and used this ratio to represent our relative compositions for the MaPI samples.

B. THz Reflection Measurements

To find carrier mobilities of our samples, we used time-resolved THz spectroscopy to measure the change in THz reflection of each sample with pump-probe measurements. For each sample, we first measured the THz signal reflected off each sample without the presence of a pump beam to excite the samples as a reference, and then measured how the reflected signal changed in the presence of a pump beam. Immediately after the pump tests, we measured the laser power at the sample through a 2 mm diameter aperture to measure the number of photons per square centimeter hitting the samples in each pulse of the pump beam. The laser power would fluctuate over the course of a day of testing, so measurements of the power at a time as close as possible to
each sample test was needed for an accurate calculation of the photon flux per pulse for a given sample.

We performed our tests on the MULE laser system at the University of Minnesota, which consisted of a pulsed Quantronix Integra laser, with a pulse rate of 1,000 pulses per second. Using a 70/30 beam splitter, 30% of the laser power went towards generating the THz beam with via another zinc telluride emitter, and 70% of the power was used for the pump beam that went through an optical parametric amplifier (OPA) that allowed us to tune the pump beam wavelength to a specific desired value. Figure 1 below shows a schematic diagram of the MULE system.

![Schematic diagram of the MULE THz reflection system. Laser path begins at the Quantronix Integra laser on the left and terminates at the differential photometer in the bottom right. Purple beam represents OPA-tuned pump beam; red beam represents THz detection and generation; and more dispersed grey beam represents THz beam.](image)

**Figure 1.** Schematic diagram of the MULE THz reflection system. Laser path begins at the Quantronix Integra laser on the left and terminates at the differential photometer in the bottom right. Purple beam represents OPA-tuned pump beam; red beam represents THz detection and generation; and more dispersed grey beam represents THz beam.
We used a pump wavelength of 650 nm; this wavelength of light carried energy higher than the MaPI bandgap and could therefore excite electrons from the valence bands to the conduction band of the sample, while also not carrying high enough energy to damage the samples. Each beam path, the THz and pump paths, included a delay stage that were used to control the timing and phase of the two beams hitting the samples, as well as to scan across a range of delays during our tests.

Our tests were run using a LabView program, and we established a common procedure for our THz reference and THz-pump tests. The THz reference tests scanned across a THz delay range of -2,000 femtoseconds to +6,000 femtoseconds, measuring with increments of 50 and with a time constant of 1 second. The THz-pump tests used the same THz delay range of -2,000 to +6,000 femtoseconds, but were averaged over 4 scans across that range, and also used the same 50 increments and 1 second time constant. The THz-pump scans were performed with the 650 nm pump beam exciting the sample, and we fixed the pump delay stage at +5,000 femtoseconds as this was high enough to reliably be past the zero delay point for the pump beam such that it was properly exciting each sample.

Each of these scans produced graphs of THz signal in millivolts versus THz delay in femtoseconds, and we recorded the value of the large peak on each graph to use in our calculation of carrier mobility.

C. Measuring Transmission and Reflection Coefficients

In addition to the change in THz reflection measured using the MULE system, we also needed the reflection and transmission coefficients for the samples at 650 nm. The carrier mobility is a measurement of how effectively photocarriers excited by pump radiation can move about the structure of the sample. One component of this measurement is the number of photons absorbed
by the sample, though that cannot be measured directly. As previously stated we used the pump beam power at the sample to find the photon flux, but only those photons absorbed by the samples generate photocarriers. Therefore, we needed to identify the percentage of 650 nm light reflected and transmitted by each sample in order to remove it from our calculations of carrier mobility.

We used a FLAME spectrometer to perform these measurements, which used a white light lamp to measure how much of the light at each constituent wavelength was transmitted in one configuration of the setup, and how much was reflected using the other. We used the data from the spectrometer to produce R-T graphs for each sample, and identified the values of the reflection and transmission coefficients at 650 nm, which we then used in calculating our carrier mobilities.

**III. Data/Results**

From our measurements of IR and THz transmission, we were able to approximate the relative compositions of our samples. Figure 2 below collects the final relative composition ratios for the samples in a bar chart.
Figure 2. A bar chart of composition ratios (lead iodide to methylammonium) by sample. The thin black line marks the separation between vapor deposited and spin coated samples.

In this chart, we can see three particularly notable features. First is that while all samples show some variation in their compositions, which is to be expected at a certain degree, the spin coated samples from groups E and F exhibit much smaller variations than the vapor deposited samples, ranging roughly between ratio values of 30 and 40. The vapor deposited samples, on the other hand, have a much larger range of composition ratios, from as low as 5 in sample B2 to as nearly 50 in sample B3. This suggests that the composition of spin coated samples is considerably more predictable and regular compared to vapor deposited samples. Looking at B2 and B3 puts into stark focus the high variance of vapor deposition composition ratios. These two samples, being part of the same group B, were made at the same time and in the same way, and even using the same conducting layer. Despite this, B2 gave the lowest ratio of lead iodide to methylammonium while B3 gave the highest, showing there is an extremely high level of unpredictability in making these samples. As previously stated, the nature of the six lettered groups of samples...
should in theory result in a very low variance in composition and performance within a single group, and while that is reflected in the spin coated E and F samples, the same is not true when looking at the compositions of the vapor deposited samples. This high variation between the compositions of the two group B samples implies a risk in the vapor deposition process for producing the samples that isn’t present in spin coating, and is important to note for further development of vapor deposition techniques.

The second factor to take note of from this graph is the extremely low ratios of lead iodide to methylammonium, relative to the rest of the samples tested, that were found for samples A3 and B2. These two have by far the highest concentrations of methylammonium out of our sample set, and that is a very important factor to bear in mind when we look at the carrier mobility data. The third factor, related to the second, is that B3’s lead iodide concentration is notably higher than all of the spin coated samples. Noting the consistent compositions of the spin coated samples, and comparing their mobilities to the vapor deposited samples – especially the three extreme cases of A3, B2, and B3 – will be very telling as to how mobility varies with composition.

From our THz reflection tests and our values of the R and T coefficients at 650 nm for each sample, we were able to calculate the carrier mobilities of each sample using the following equation:

\[
\mu = \frac{\sigma}{e\phi_\gamma (1 - R)(1 - T)} \quad \text{(Eq. 1)}
\]

Here, \(\mu\) is the carrier mobility; \(\sigma\) is the change in surface conductivity of the sample under excitation by the pump beam in \(\Omega^{-1}\); \(e\) is electron charge; \(\phi_\gamma\) is the photon flux at the sample in photons/cm\(^2\)/pulse; and R and T are respectively a sample’s reflection and transmission coefficients, each for light with wavelength of 650 nm.
Change in surface conductivity \( \sigma \) was calculated using our data from the MULE THz spectroscopy tests. We took the ratio of the THz-pump peak signal to the THz reference peak, and used a LabView program made by Professor Heyman that took in that ratio and used the Drude model to return a value for \( \sigma \).

Photon flux \( \phi_\gamma \) was calculated using our measurements of the pump beam’s power at the end of each sample test through a 2 mm-diameter aperture, the pump beam’s wavelength of 650 nm, and the pulse rate of the Quantronix Integra system. These calculations were done with the following equation:

\[
\phi_\gamma = \frac{P}{(\pi \times 10^{-2} \text{ cm}^2)(1000 \text{ pulse/s})} \cdot \frac{650 \text{ nm}}{e(1240 \text{ eV} \cdot \text{nm})}
\]  

(Eq. 2)

Here, \( P \) is the power of the pump beam in W and \( e \) is again the electron charge. Table 1 below contains our measured values of THz and THz-pump peak signals, pump power, and reflection and transmission coefficients for 650 nm light, while Table 2 below contains the calculated values for surface conductivity, photon flux, and carrier mobility, for each sample.

**Table 1.** Experimentally measured values for each sample: THz and THz-pump peak signals, pump power at sample, and reflection and transmission coefficients at 650 nm. Some samples were tested twice to check for measurement reproducibility and carrier mobility error.

<table>
<thead>
<tr>
<th>Sample</th>
<th>THz Peak (mV)</th>
<th>THz-Pump Peak (mV)</th>
<th>Pump Power (W)</th>
<th>R [650 nm]</th>
<th>T [650 nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>6.3</td>
<td>0.9</td>
<td>0.0015</td>
<td>0.16</td>
<td>0.07</td>
</tr>
<tr>
<td>A3</td>
<td>6.8</td>
<td>0.26</td>
<td>0.0017</td>
<td>0.13</td>
<td>0.12</td>
</tr>
<tr>
<td>B2 (1)</td>
<td>6.0</td>
<td>0.26</td>
<td>0.0016</td>
<td>0.15</td>
<td>0.21</td>
</tr>
<tr>
<td>B2 (2)</td>
<td>5.8</td>
<td>0.25</td>
<td>0.0013</td>
<td>0.15</td>
<td>0.21</td>
</tr>
<tr>
<td>B3 (1)</td>
<td>6.8</td>
<td>0.69</td>
<td>0.0017</td>
<td>0.19</td>
<td>0.13</td>
</tr>
<tr>
<td>B3 (2)</td>
<td>6.0</td>
<td>0.70</td>
<td>0.0016</td>
<td>0.19</td>
<td>0.13</td>
</tr>
<tr>
<td>C2</td>
<td>6.7</td>
<td>0.84</td>
<td>0.0013</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>C3</td>
<td>7.4</td>
<td>0.88</td>
<td>0.0016</td>
<td>0.23</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Table 2. Calculated values for each sample: change in surface conductivity, photon flux at the sample, and carrier mobility. Some samples were tested twice to check for measurement reproducibility and carrier mobility error.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma$ ((\Omega^{-1}))</th>
<th>$\phi_p$ (photons/cm(^2)/pulse)</th>
<th>$\mu$ (cm(^2)/V*s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>8.34 $\times 10^{-4}$</td>
<td>1.56 $\times 10^{14}$</td>
<td>43</td>
</tr>
<tr>
<td>A3</td>
<td>2.34 $\times 10^{-4}$</td>
<td>1.77 $\times 10^{14}$</td>
<td>11</td>
</tr>
<tr>
<td>B2 (1)</td>
<td>2.23 $\times 10^{-4}$</td>
<td>1.67 $\times 10^{14}$</td>
<td>12</td>
</tr>
<tr>
<td>B2 (2)</td>
<td>2.23 $\times 10^{-4}$</td>
<td>1.35 $\times 10^{14}$</td>
<td>15</td>
</tr>
<tr>
<td>B3 (1)</td>
<td>0.616 $\times 10^{-4}$</td>
<td>1.77 $\times 10^{14}$</td>
<td>31</td>
</tr>
<tr>
<td>B3 (2)</td>
<td>7.66 $\times 10^{-4}$</td>
<td>1.67 $\times 10^{14}$</td>
<td>41</td>
</tr>
<tr>
<td>C2</td>
<td>7.85 $\times 10^{-4}$</td>
<td>1.35 $\times 10^{14}$</td>
<td>57</td>
</tr>
<tr>
<td>C3</td>
<td>6.85 $\times 10^{-4}$</td>
<td>1.67 $\times 10^{14}$</td>
<td>38</td>
</tr>
<tr>
<td>D2</td>
<td>6.85 $\times 10^{-4}$</td>
<td>1.35 $\times 10^{14}$</td>
<td>43</td>
</tr>
<tr>
<td>E2</td>
<td>8.87 $\times 10^{-4}$</td>
<td>1.35 $\times 10^{14}$</td>
<td>67</td>
</tr>
<tr>
<td>E3 (1)</td>
<td>9.17 $\times 10^{-4}$</td>
<td>1.67 $\times 10^{14}$</td>
<td>57</td>
</tr>
<tr>
<td>E3 (2)</td>
<td>9.05 $\times 10^{-4}$</td>
<td>1.56 $\times 10^{14}$</td>
<td>60</td>
</tr>
<tr>
<td>F1</td>
<td>8.59 $\times 10^{-4}$</td>
<td>1.67 $\times 10^{14}$</td>
<td>52</td>
</tr>
<tr>
<td>F2</td>
<td>7.88 $\times 10^{-4}$</td>
<td>1.25 $\times 10^{14}$</td>
<td>51</td>
</tr>
</tbody>
</table>

Based on our reproducibility tests, our carrier mobility values have an uncertainty of ±25%. This uncertainty is simply taken from the maximum variance between mobility values obtained for a single sample, which was for B3. This is quite large, so one goal of future work on this project would be to refine our system to reduce this uncertainty. This could be done by refining and streamlining our measurement process, specifically with respect to regulating the way the pump beam excites the sample. Another source of uncertainty is water in the air that the lasers pass through. To minimize this all of our measurements are performed within a vacuum purge.
chamber, but this could be further reduced by somehow improving the seal on the chamber or increasing the purge time between each test.

Figure 3 below is another bar chart, this time charting the carrier mobilities of each of our samples.

![Figure 3. A bar chart of calculated carrier mobility values for each sample. The thin black line marks the separation between vapor deposited and spin coated samples. For samples that were tested twice, mobility values from both tests are included.](image)

Looking at the columns in Figure 3, we can see right away that once again the spin coated samples are all clustered together with similar mobility values – but not only that, since they also have generally higher mobilities than the vapor deposited samples with one exception. We can also see that samples A3 and B2, the ones with the highest concentrations of methylammonium, also have by far the lowest carrier mobilities, which would suggest too much methylammonium in the MaPI film reduces carrier mobility. However, we can get a better picture by plotting the carrier mobilities against the composition ratios, as in Figure 4 below.
Figure 4. A plot of sample carrier mobility versus composition ratio (Pb-I:N-H band strengths) with error bars. Shows a peaked relationship between the two. Composition ratios have been normalized around sample E3, and certain noteworthy samples have been labeled explicitly. Spin coated samples are represented by red squares, and vapor deposited ones by black circles.

Looking at this graph, we can see much more clearly the relation between these two values. First and foremost is that the carrier mobilities follow a peaked distribution with respect to the composition ratio of lead iodide to methylammonium. In other words, there is some ideal ratio of these two components in MaPI samples that maximizes the resulting solar cell’s carrier mobility. Focusing our attention on the highest values on this plot we can see that the spin coated samples in groups E and F are all clustered near the top of this distribution, seemingly on either side of the peak. So the spin coated samples, which had lower variation in their composition ratios, were
also the samples that performed the best. This doesn’t mean the vapor deposited samples are necessarily bad, however. As mentioned earlier, one vapor deposited sample had a mobility that was on par with the spin coated samples, and that was C2. From this graph, we can see that it is located close to the peak of the mobility distribution, comfortably within the spread of the spin coated samples, and has a Pbl:Ma ratio that is also very similar to those other best-performing samples. Just as in the composition bar chart we see the same wider variation in composition and mobilities among the vapor deposited samples, but when their composition matches up to the spin coated samples, as is the case with C2, it performs just as well as they do.

We can also take note of our compositional exceptions of A3, B2, and B3. The former two, with their high methylammonium concentrations and low carrier mobilities, are located far to the bottom left of the peaked distribution. B3 on the other hand, which we noted as having a higher lead iodide concentration than any of the spin coated samples, also had a lower carrier mobility than those samples. Being lower and to the right of the peak in our distribution, this sample is in large part what tells us that this is a peaked distribution. The samples with the highest carrier mobilities were not those with the highest concentration of methylammonium (A3, B2) or of lead iodide (B3), but somewhere closer to the middle. It is then clear that it is a specific balance of these two components that maximizes the performance of the MaPI solar cells, rather than one being more playing a clearly more important role than the other.

**IV. Summary/Conclusions**

In summary, we performed our research in collaboration with the Holmes research group; they made MaPI perovskite solar cell samples and we characterized them. We used THz and IR transmission measurements to find the relative ratio between the lead iodide and methylammonium concentrations of the samples, and time resolved THz spectroscopy to study
the surface conductivity of the samples, which in turn allowed us to calculate their carrier 
moilities. We found that vapor deposited samples had a much higher variance in their 
compositions than spin coated samples, even within a production batch as in the case of B2 and 
B3. Comparing our results for composition ratios with the samples’ mobility values we found a 
peaked distribution of mobility as it relates to the PbI:Ma concentration ratio, with the less 
compositionally varied spin coated samples clustered around the peak of that distribution. Vapor 
deposited samples could be found on either side of the distribution peak, having higher than ideal 
concentrations of either methylammonium or lead iodide, which is what tells us that there exists 
an ideal ratio between the two components that would maximize sample mobility. However, we 
also saw that the vapor deposited samples weren’t inherently bad; vapor deposited C2 had a 
similar composition and carrier mobility to those of the less varied spin coated samples. So when 
vapor deposited samples strike close to that ideal balance between lead iodide and 
methylammonium, they perform just as well as the spin coated ones; it’s simply a question of 
whether the vapor deposition process can be tuned to gain more control of the sample 
compositions.

Future work on this project includes a more focused and exact test of composition’s effects on 
 mobility using a set of spin coated samples made with intentionally varied compositions; further 
tests of how vapor deposited and spin coated samples perform relative to each other after more 
thoroughly answering the composition question; and studying the effects of inhomogeneity on a 
samples’ surface on its mobility values.
V. References
