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Article 1

Carrier Mobility of Bismuth-Doped Perovskite

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Abstract

As renewable energy increasingly becomes a priority around the world, the demand for inexpensive, efficient solar cells is greater than ever. Lead halide perovskites show promising potential, but have their share of drawbacks that could be improved through slight changes to its elemental composition. We used time-resolved terahertz spectroscopy to probe the differences created by doping lead halide perovskites with bismuth. We found that all samples, regardless of bismuth content, had a recombination time longer than one nanosecond, and that charge-carrier mobility decreased with the addition of bismuth.

Carrier Mobility of Bismuth-Doped Perovskite

Cover Page Footnote
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Introduction

With the growing concern for climate change, efficient and affordable renewable energy is becoming increasingly important. The production of thin-film solar cells is theoretically much less expensive than crystalline silicon solar cells, but often include rare elements that could drive up costs when produced in bulk. However, perovskites are a recent addition to thin film solar cells that are inexpensive and have a lot of potential [1].

Even though they were introduced in 2009 [2], the efficiency of perovskite solar cells has already grown past 20%. While this is a remarkable development for such a short amount of time, silicon solar cells are still significantly more efficient at 25%. Though perovskites have their own problems that currently make them infeasible for mass-use, such as instability over longer time frames, there are quite a few features of these solar cells that make them more appealing than silicon ones. For example, silicon cells are thicker and stiff, whereas thin-film solar cells such as perovskite ones are flexible. Additionally, perovskite solar cells are created by depositing a film onto a backing, which is much simpler than the crystalline silicon generation process, which requires the material to be super pure.

The aspect of perovskites that makes them useful for solar cells is their nature as a semiconductor. When a semiconductor is given extra energy, such as when light hits it, electrons from the full valence band, the highest energy level that still has electrons, move up to the empty conducting band, the lowest energy level that does not have electrons, allowing them to move across the surface and make the material conductive. How conductive the material becomes depends on a few characteristics, including the charge-carrier mobility and the recombination time. The carrier mobility describes how freely an individual charge can move, whereas the

recombination time describes how long the charge will be able to stay in the conducting band before falling back to the valence band. This paper describes our investigation of the effect adding bismuth to a perovskite has on the perovskite's carrier mobility.

Methodology

We were provided a total of eight samples by Lawrence Berkeley National Laboratory. The perovskites we studied had the elemental makeup $CH_3NH_3PbI_3$, doped with four different amounts of bismuth: 0.01%, 0.25%, 0.5%, and 1%. We were provided with two sets of these, and an additional sample with no bismuth was also studied as a control. This means that our samples had a small amount of Bi atoms inserted in a way that would altered some of the properties of the perovskite without changing the basic structure.

Our handling of the samples was complicated by their sensitivity to air. When outside of a nitrogen or helium environment they degraded, turning from a dark brown color to yellow and making the material less responsive to added energy. To combat this, we kept the samples in a nitrogen-filled glove bag while not being measured, and in a nitrogen or helium-filled cryostat while being measured. Despite our efforts, one of the samples with 0.01% bismuth had degraded before we first opened the case it arrived in and so was unusable.

In order to find the carrier mobilities of the samples, we had to calculate both the change in conductivity and the number of electrons that moved to the conducting band to cause that change. To find the change in conductivity we used a FemtoLaser XL-500 Ti Sapphire Laser with a wavelength of 800 nm to excite the sample, then probed the same spot on the sample with THz radiation. A diagram of our set up is included in (Figure 1). The more conductive a material

is, the less THz radiation is transmitted. Therefore, by measuring the change in transmitted THz radiation immediately before and after excitation of the sample, we can find the change in conductivity with the following equation:

$$\Delta\sigma = -\Delta t/\alpha \quad (1)$$

where σ is conductivity, t is transmission, and α is a constant. With slight alterations to the mirrors controlling the THz radiation, we can change when it hits the sample relative the 800 nm beam, giving us change in transmission as a function of time as shown in (Figure 2) [3].

To find the number of electrons, we needed to figure out how much of the 800 nm light was absorbed by the perovskite as opposed to transmitted or reflected. To do this we used a spectrometer, producing a graph of the light transmitted and light reflected by wavelength (Figure 3). 100% minus both of those results at 800 nm gives us the percent of the laser being absorbed. Because energy from light is carried in photons, which are discrete packets of energy determined by the wavelength of the light, we know that the number of photons absorbed is the same as the number of electrons elevated to the conduction band. We can then measure the area of the sample the laser hits as well as the power per laser pulse at that spot and use those values as well as the energy per 800 nm photon to determine the number of photons that are absorbed, and therefore the number of electrons that are excited.

Once we have both the change in conductivity and the number of electrons that create that conductivity all that is needed to find the carrier mobility is a simple calculation:

$$\mu = \frac{\Delta\sigma}{ne} \quad (2)$$

Other data recorded includes qualitative data about the samples and how they and their measurements change over time.

Results & Discussion

Our final results show that increasing the amount of bismuth integrated into the perovskite consistently reduces the charge-carrier mobility of the sample (Table 1). While we were not able to obtain a reliable carrier mobility for a sample with 0.01% bismuth, which would have given us another data point and therefore more insight into the trend of diminishing carrier mobility, there is still information that can be extracted beyond that the introduction of bismuth causes a loss of carrier mobility. The change in carrier mobility between the 0.25% and 0.50% samples is larger than the change between the 0.50% and 1.00% samples, despite the second comparison having twice as large a change in bismuth content. This shows that after a certain point, adding more bismuth has a diminishing effect on the change in carrier mobility per bismuth atom.

Through measuring the THz transmission results, we also made observations about the recombination time, another aspect that contributes to conductivity. Extending the amount of time the measurement covered showed little change in THz transmission, meaning the recombination time of all of the samples was greater than 1 ns. Because the result was too large for our system to measure, we were unable to tell if the addition of bismuth had any effect on this characteristic. This also meant that the number of electrons excited did not return to zero by the time the next measurement was taken, but that did not affect our measurements of change in conductivity because we measure the change in transmission from immediately before the pump pulse hits and immediately after, and the number of electrons elevated to the conduction band would be unaffected by the number already there.

While we were able to successfully take THz transmission measurements for most of the samples, the change in transmission was on the small end of what our system was able to reliably record. This was due in part to the relatively low level of absorption of 800 nm light exhibited by the samples. Efforts to achieve a larger reading that would have been easier to separate from random noise included frequency-doubling the laser used to excite the sample, as a higher percentage of 400 nm light was absorbed, but this sped up the degradation of the sample to the point where the diminishing of change in transmission was visible in the data from consecutively taken measurements. This degradation was visible on the sample as a yellow area on the film where the laser had been hitting it, making it clear that the light itself caused it, not just an exposure to air. In response we switched to testing the samples in a helium environment to reduce any chemical changes the excitation might cause, and saw a reduction in rate of degradation, though not a massive one. Because it was still impossible due to degradation to reproduce the initial measurement taken from a point on the sample with a consecutive measurement, we switched back to using 800 nm light, though we continued using helium in the testing environment.

We were able to obtain results we were confident in through the use of repeated measurements, averaging the result until we could discern a clear change in transmission that we could separate from the noise. While these measurements individually were less definitive than the ones taken using 400 nm light, the ability to complete multiple measurements that showed similar results was more valuable. Even so, each sample could only be tested for a few hours before the point on its surface hit by the later was damaged enough to affect the THz transmission results.

Because it took time to discover the most accurate and reliable methods to obtain the THz transmission and 800 nm light absorption measurements, the first set of samples had already experienced significant degradation by the time those methods were established. Previous measurements and inadvertent exposure to air had affected them visibly, and beyond the clearly yellow spots from the laser they were overall slightly lighter in color than the second set, which we had found over the course of our research to mean the change in conductivity had also degraded. Because of this we set aside these measurements and relied on the measurements of the second set, taken quickly after their release from long-term storage. The second set of samples had, overall, a significantly higher rate of measured absorption, which we believe shows that the first set had in fact degraded. Unfortunately, the sample doped with 0.01% bismuth in the second set had clearly suffered degradation at the time we opened its storage container, so we were not able to obtain reliable results for either 0.01% sample. Despite this, the trend towards diminishing carrier mobility is comfortably reliable.

Summary & Conclusions

Doping $CH_3NH_3PBI_3$ with bismuth has one clear effect: lowering the carrier mobility. An average carrier mobility for undoped perovskite is around 6 cm^2/Vs, you can see in Table 1 that the result for even just 0.25% bismuth was a third of that. Whatever other effect the addition of bismuth might have, such a steep reduction in carrier mobility makes this material unsuitable for use in a solar cell.

While we were not able to judge how the recombination time was affected due to it being longer than what we were able to measure for all samples, there is other knowledge that can be

taken from our research. The fact that the rate of degradation when the sample was exposed to the laser slowed when we switched the environment from nitrogen to helium, a noble gas, shows that the cause of some, but not all, of the degradation is chemical. It is also possible that the transmission spectrum of a very degraded sample (Figure 4) could help inform how the degradation is actually changing the sample, and what is causing it.

References

[1] Hodes, Gary. "Perovskite-Based Solar Cells." *SCIENCE*, 18 Oct. 2013, pp. 317–318.

[2] Loi, Maria Antonietta, and Jan C Hummelen. "Perovskites Under the Sun." Nature Materials, Dec. 2013, pp. 1087–1089.

[3] Redo-Sanchez, Albert. "The Terahertz Wave EBook." The Terahertz Wave EBook, Zomega Terahertz Corporation, 2012, pp. 6–9.

Tables and Figures

Bismuth Percent	Carrier Mobility (cm^2/Vs)
0.25%	1.912
0.50%	1.198
1.00%	0.634

Table 1. The carrier mobilities of our second set of samples. From top to bottom, the samples are 0.25% bismuth, 0.50% bismuth, and 1.00% bismuth.

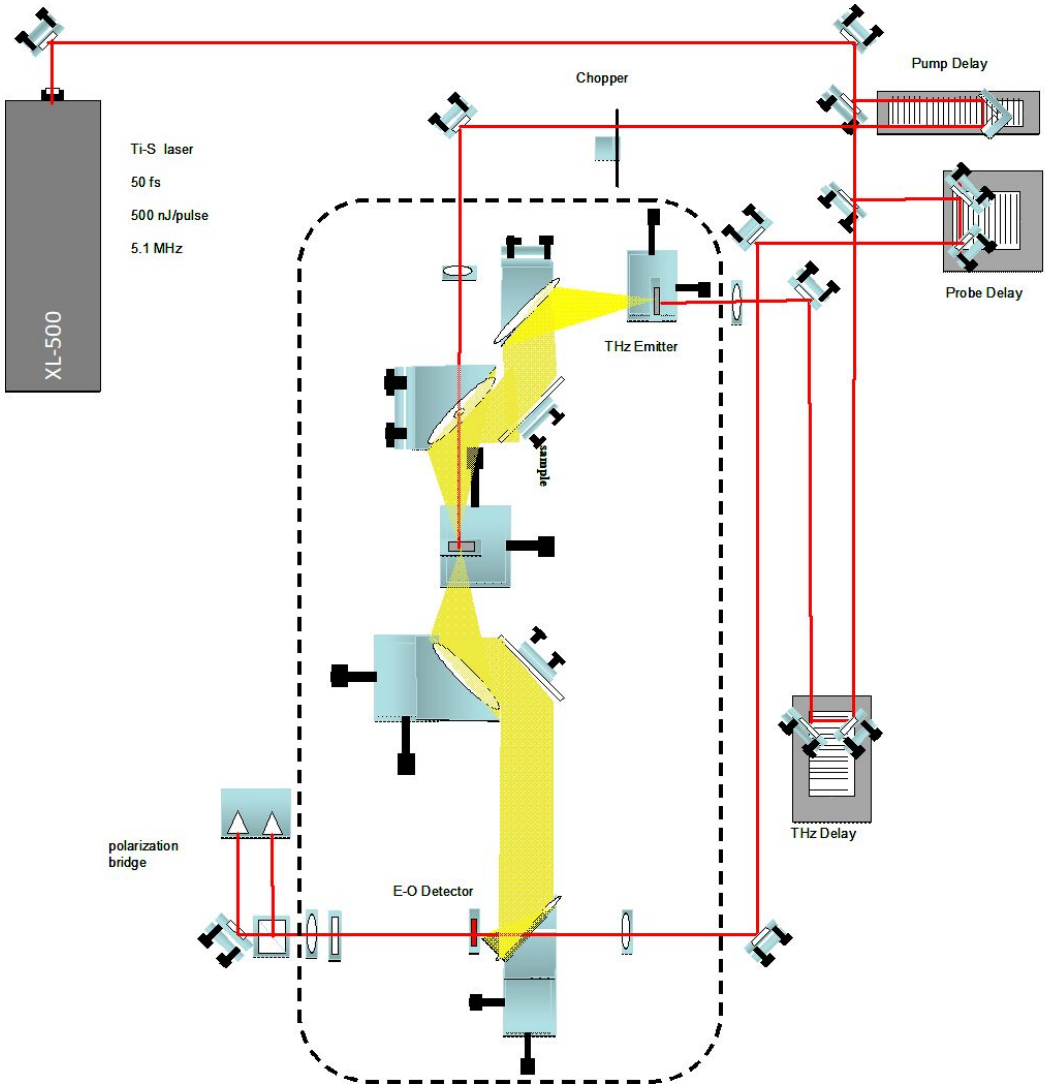

Figure 1. A diagram of the laser system. A yellow beam represents terahertz radiation, a red beam represents 800 nm light. The sample is located at the small grey rectangle in the center of the diagram.

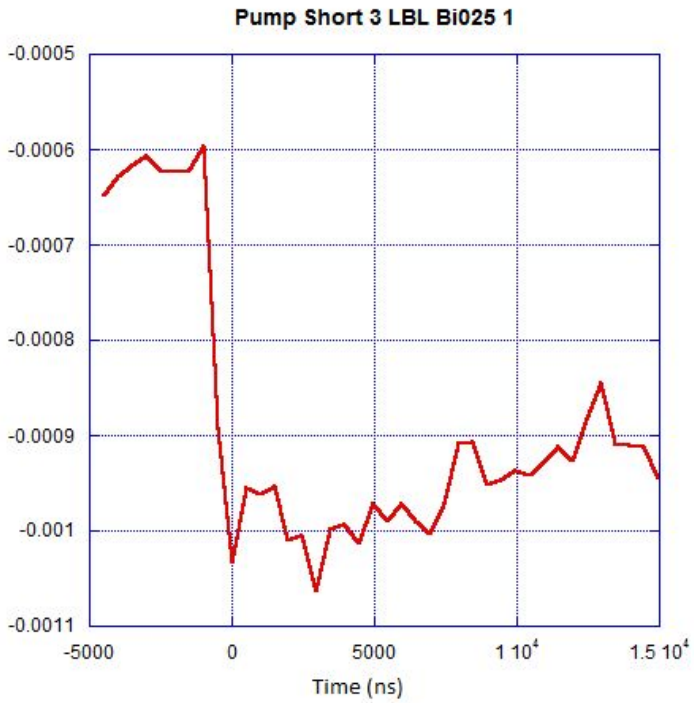

Figure 2. THz transmission measurements of a sample with 0.25% bismuth. Change in THz transmission on the y axis and time elapsed in femtoseconds since the pump beam hit the sample on the x axis.

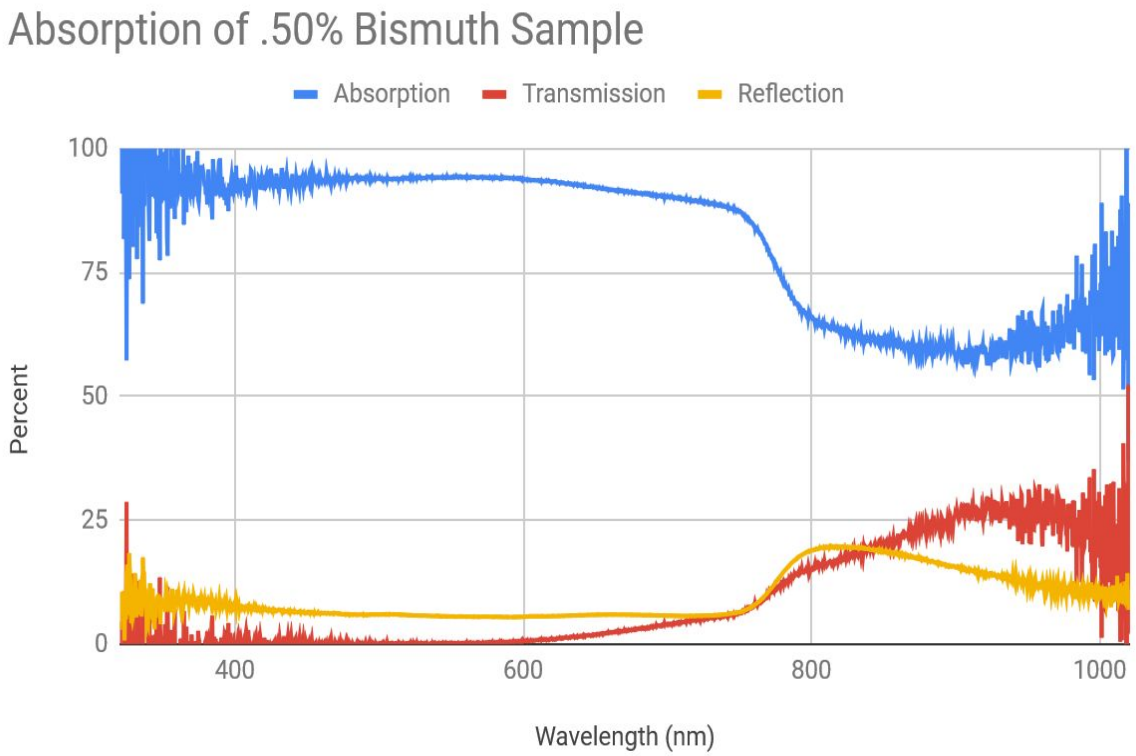

Figure 3. This is the transmission and reflection graph of a sample with 0.50% bismuth. Percent of light transmitted (red), reflected (yellow), or absorbed (blue) on the y axis, wavelength of incident light on the x axis. The value significant to us is the one at 800 nm. Tests at 400 nm were also tried due to the higher level of absorption at that wavelength, but were too damaging to the sample to continue.

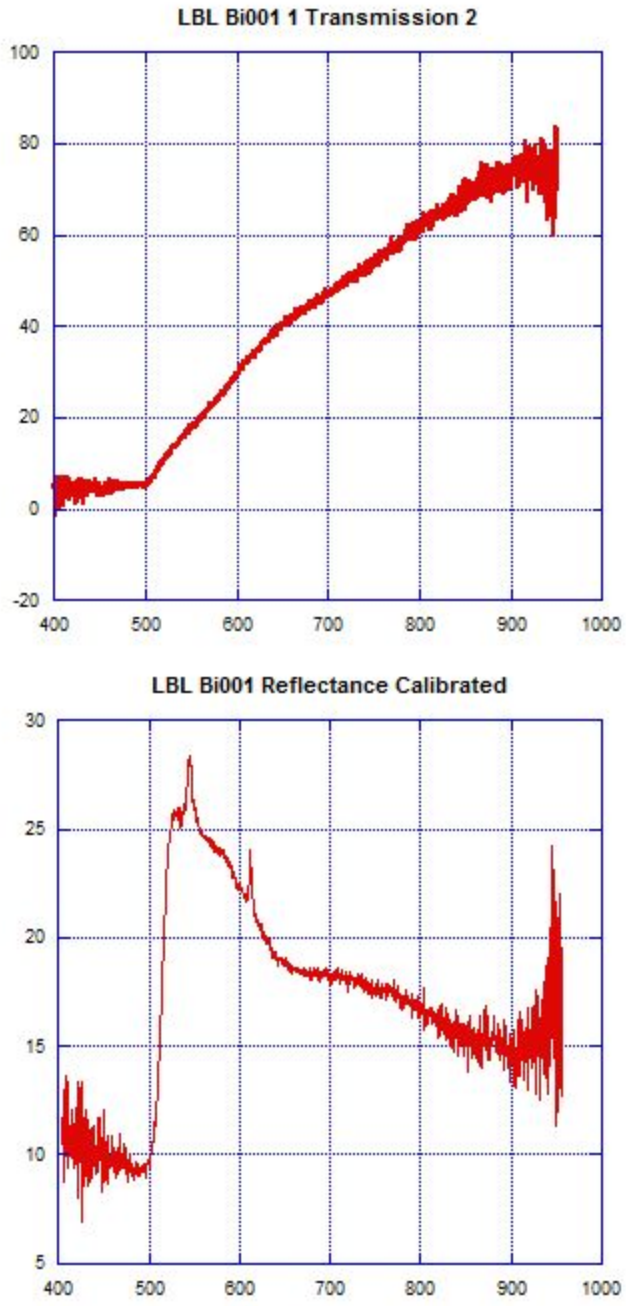

Figure 4. Transmission and reflection graph of a degraded sample. Percent of light transmitted (upper) or reflected (lower) on the y axis, wavelength of incident light on the x axis. Compared to Figure 2, transmission has increased on all wavelengths, the bandgap completely vanished. The reflectance has also shifted to be higher at smaller wavelengths.