How 2D – 3D Crystal Formation Affects Carrier Mobility and Lifetime in Perovskite Solar Cells

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Introduction

Hybrid organic-inorganic semiconductors called perovskites are promising solar cell materials. They have achieved photo-conversion efficiencies higher than 20% in recent years, and are simple and cheap to fabricate. However, the most efficient perovskite solar cells contain lead and are unstable under exposure to water, heat, and light. Moisture resistant and lead-free perovskites do exist, but they tend to form in 2D or lower dimension crystal structures with far lower efficiencies.

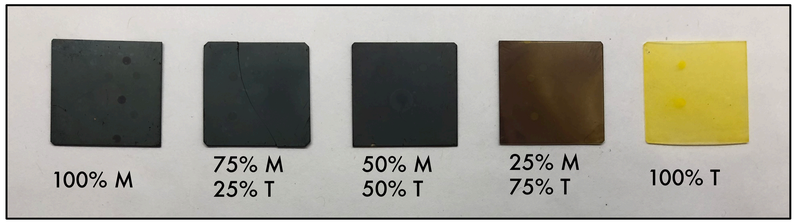


Figure 1 Photograph of all five samples in series. From left to right, power conversion efficiencies are 10.2%, 5.3%, 0.3%, 0.3%, and 0.1%.

Using time-resolved terahertz spectroscopy on a set of 2D – 3D perovskite samples, we examine how mobile electrons are and how long they remain excited after photoexcitation.

2D – 3D Sample Series

A perovskite crystal structure requires a large cation, a small cation, and an anion; in our 3D samples, these are methylammonium (M), lead (Pb), and iodine (I).

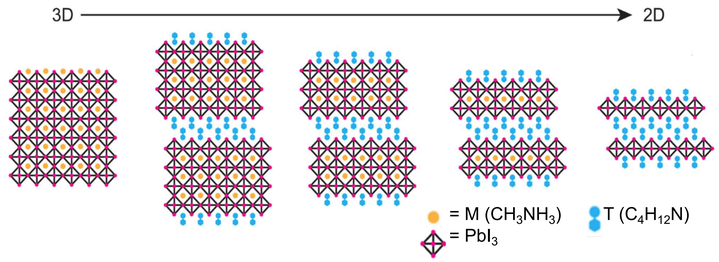


Figure 2 Illustration of perovskite layer thickness (between layers of organic material) as crystal transitions from 3D to 2D[1]

To create 2D materials, we replace M with fractions of t-butylammonium (T), a much larger organic molecule, from 25 to 100 percent. This causes the perovskites to form in alternating sheets of organic material, T and $MAPbI_3$ or PbI_3, with thickness determined by ratio of M to T.

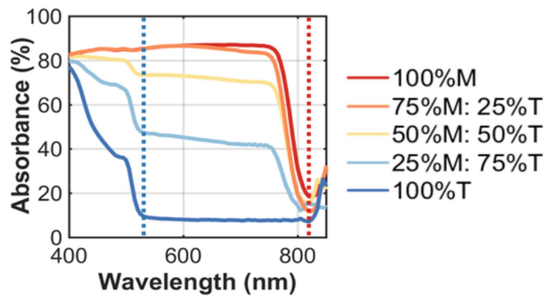


Figure 3 Light absorption data for samples in the 2D-3D series

Experimental Setup

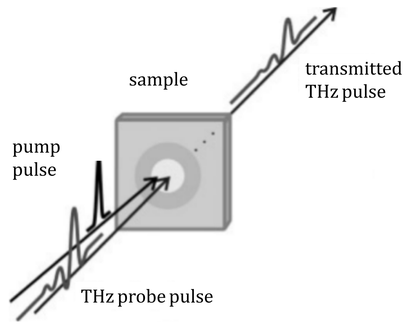


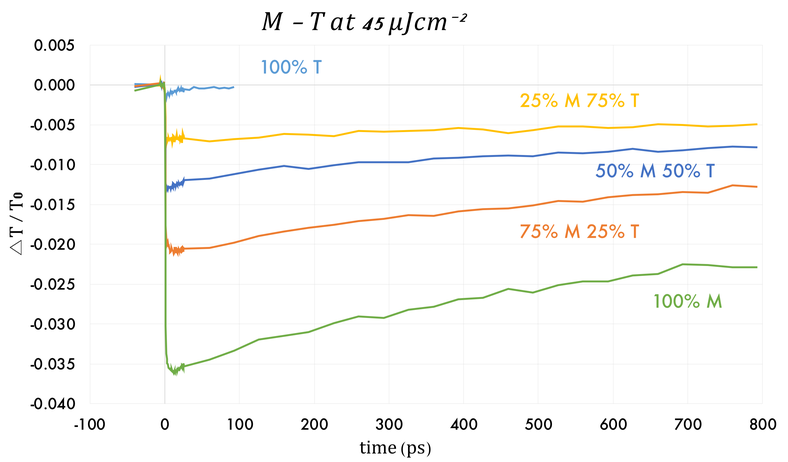
Figure 4 Interaction between pump, probe, and sample[2]

We excite each sample with a 400 nm pump and measure transmission of a 1.2 THz probe on picosecond timescales—the more conductive a sample becomes, the less THz it transmits.

$$\Delta\sigma \sim \frac{\Delta T}{T_0}, \quad \Delta\sigma = q\,\phi\mu\,\Delta n(t)$$

Effective charge carrier mobility ($\phi\mu$) at a given fluence is proportional to change in THz (ΔT) after excitation divided by initial THz (T_0). Measurements over a range of times after excitation give us charge carrier lifetimes.

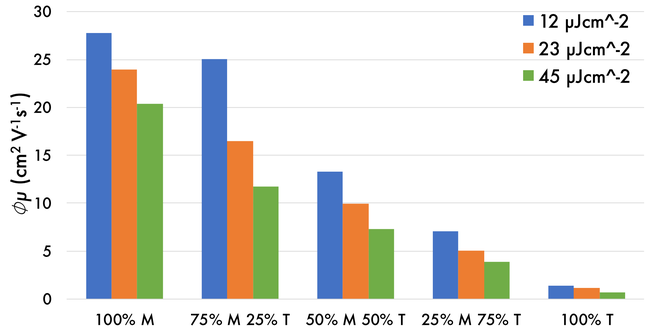
Results: Carrier Lifetime



- Charge carrier lifetime appears longest for our 25% M 75% T sample, followed by the other 2D – 3D hybrid samples. Other literature proposes that lifetime should decrease with increasing 2D character due to increased excitonic activity,[1] but we observed that lifetime increased with the addition of 2D material and then sharply decreased for material which was completely 2D.
- Blancon et al propose that having a fraction of 2D material in perovskite thin films can create an efficient mechanism for exciton dissociation across internal crystal boundaries;[3] this mechanism could explain the increased charge carrier lifetimes we see here.

Results: Carrier Mobility

Mobility at 3 Fluences



- Effective mobility ($\phi\mu$) declines with increased 2D character due to the confinement of charge conduction within inorganic layers. We use ϕ to account for the fraction of photons converted into free charge-carrier pairs rather than excitons.
- $\phi\mu$, along with charge carrier lifetime, decreases with increased fluence for all five samples. Higher excitation density effectively increases impurity concentration, restricting charge carrier movement.

Conclusions and Future Work

- Since mobility consistently increased at lower fluences for all five samples, we wonder which fluence could give us maximum mobility.
- We plan to investigate how excitonic activity in these hybrid materials might be contributing to the unexpectedly long lifetimes we see in 2D – 3D transitional samples.
- Perhaps, through the addition of small amounts of 2D material to a 3D perovskite, we could maximize a mobility-lifetime product to improve solar cell performance.
- Fitting models to these lifetime curves will allow us to extract monomolecular, bimolecular, and Auger recombination rates for each material.
- Based on XRD, PL and absorption data, it appears as though our transitional samples might be segregated into sections of 2D and 3D material rather than uniformly layered according to the Ruddleston-Popper model. This brings into question whether our data is illustrating behaviors of different 2D-3D structures, or different contributions from 2D and 3D sections.

References

[1] Milot, Rebecca L., et al. Nano Lett 16, 7001–7007, (2016).

[2] Hegmann, Frank A., et al. *Photophysics of Molecular Materials : From Single Molecules to Single Crystals*. Wiley, 2006. 396.

[3] Blancon, J. –C., et al. *Science* 355, 1288–1292, (2017).