How Modifications to Perovskite Composition Impact Carrier Mobility and Lifetime in Solar Cells

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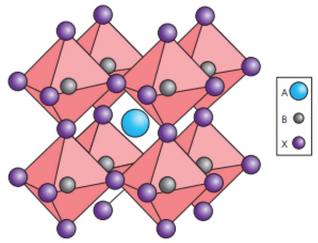
Introduction

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, are unstable under exposure to water, heat, and light, and exhibit an effect called hysteresis, which leads to inconsistent solar cell performance. Perovskite crystal structure includes a large cation (methylammonium), a small cation (lead), and an anion (iodine), as illustrated in figure 1. Each of these three components can be modified to improve material quality or suppress hysteresis, but changes to perovskite structure often compromise solar cell performance.



We focus on two different techniques of modifying perovskite composition, addressing hysteresis and lead content, respectively. We use time-resolved terahertz spectroscopy to examine how mobile electrons are and how long they remain excited after photoexcitation, to help determine how solar cells will perform. We also use scanning electron microscope (SEM) imaging to study how compositional changes affect crystal morphology.

Figure 1 Illustration of an ideal perovskite crystal structure ($MAPbI_3$), with large cation A, small cation B, and anion X.[1]

Rubidium and Cesium Series: Mobility and Lifetime

Replacing small amounts of MA with inorganic rubidium (Rb) atoms, which are significantly smaller than MA molecules, has been shown to reduce hysteresis effects, however the mechanism is not well understood. Here, we compare Rb-doped samples to samples doped with cesium (Cs), a slightly larger inorganic atom which has not been shown to reduce hysteresis to nearly the same extent, in order to clarify why Rb is so effective.

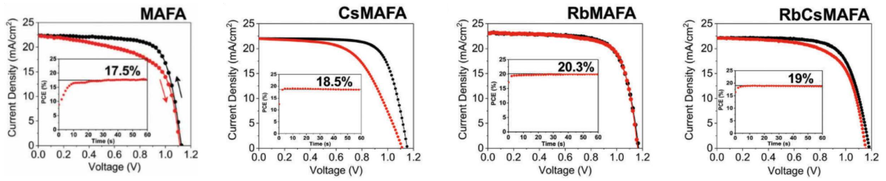


Figure 2 J-V curves illustrating hysteresis reduction with the addition of Rb[2]

We first took time-resolved terahertz spectroscopy (TRTS) measurements on a series of seven samples of doping concentrations from 1% to 5%, which we used to extract charge carrier mobility and preliminary lifetime measurements for these samples.

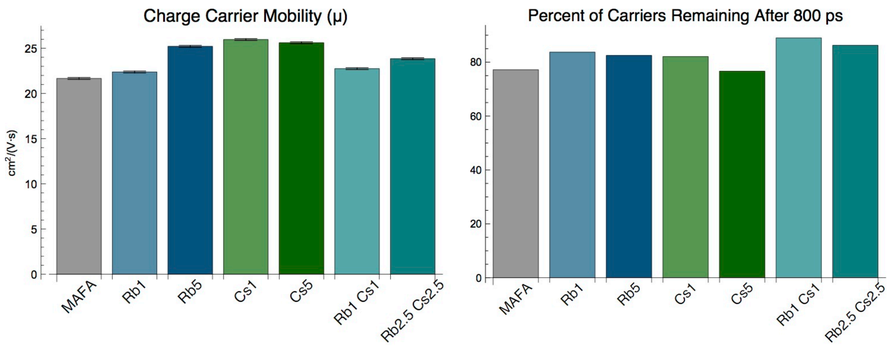


Figure 3 Bar graphs illustrating our results from TRTS

Rubidium and Cesium Series: SEM Images

After noticing improvements in mobility and lifetime with the addition of Rb and Cs dopants, we used SEM imaging to investigate whether we could link these improvements in performance to changes in morphology, such as increased grain size or reduced crystallite formation.

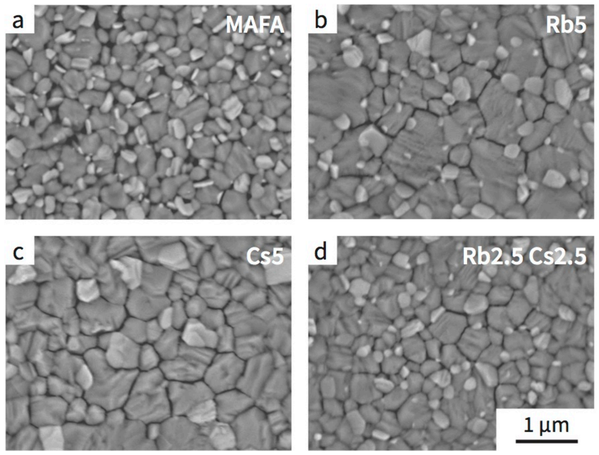


Figure 4 SEM images taken of four samples in our series. We used back scattering electron (BSE) detection to help us distinguish between $MAPbI_3$ crystals and Pb-rich crystallites

Lead-Free Series: Mobility and Lifetime

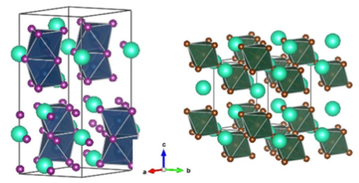


Figure 5 Illustration of 0D ($A_3B_2I_9$) and 2D ($A_3B_2Br_9$) lead-free perovskite structures[3]

Replacing all of the Pb in a perovskite sample with a different small cation alters perovskite composition and structure. Because changing the radius of the B component changes the ratios between crystal components, leading to deviations in crystal structure, many lead-free perovskite formulas also replace MA or I with other large cations or anions.[3] Here, we work with $MA_3Bi_2I_9$, which gives us optimal light absorption but has a 0D structure, $MA_3Sb_2Br_9$, which has a 2D structure with less optimal absorption, and a 2D 6:4 hybrid of the two.

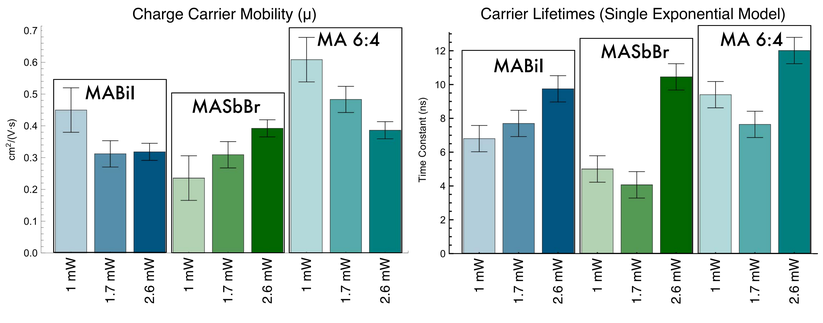


Figure 6 Bar graphs illustrating our results from TRTS

Lead-Free Series: SEM Images

Our collaborators have been working to optimize crystal growth in their fabrication of lead-free samples, despite somewhat unpredictable crystal structures. We took SEM images to determine how crystals were forming and whether 2D crystal 'sheets' were oriented parallel to the substrate.

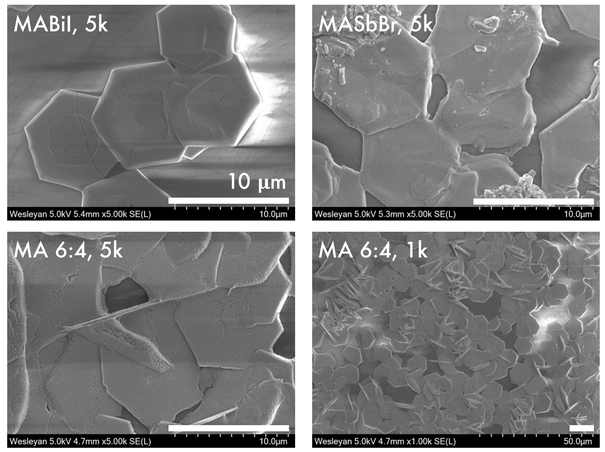


Figure 7 SEM images of our three lead-free samples at 5k magnification, as well as our hybrid sample at 1k to illustrate structure on a larger scale

Conclusions and Future Work

Rubidium and Cesium Series

- We see improvements in both mobility and lifetime with the introduction of any Rb and/or Cs doping. Cs doping optimizes mobility, while hybrid doping appears to optimize lifetime.
- We can conclude that neither increased charge carrier mobility nor increased lifetime is directly correlated to reduced hysteresis.
- We also observe that although doping does increase crystal grain size somewhat, it does not suppress crystallite formation.

Lead-Free Series

- We can see that both lifetime and mobility are optimized in the hybrid sample, although there is some variation in how the three samples respond to changes in pump fluence.
- SEM imaging seems to indicate that crystal formation is oriented parallel to the substrate. With better grounding techniques, we could look for defects at higher magnification.
- We may need to modify our mobility calculations to account for low absorption in 2D samples.

References

[1] Green, Martin A., et al., Nature Photonics 8.7 (2014): 506-514

[2] Turren-Cruz, Silver-Hamill, et al. Energy Environ. Sci. (2018): 78-86

[3] Sun, Shijing, et al., Joule (2019):1437-1451