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The Effect of *Tert*-butylammonium Addition in Methylammonium Lead Iodide Perovskite Solar Cells

Noor Titan Putri Hartono,[1] Shijing Sun,[1] María Gélvez-Rueda,[2] Polly Pierone,[3] Matthew Erodici,[3] Jason Yoo,[1] Fengxia Wei,[4] Moungi Bawendi,[1] Ferdinand Grozema,[2] Meng-ju Sher,[3] Tonio Buonassisi,[1] Juan-Pablo Correa-Baena[1]

[1]Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA, 02139, USA
[2]Delft University of Technology, van der Maasweg 9, 2629 HZ Delft, The Netherlands
[3]Wesleyan University, 265 Church Street, Middletown, CT, 06459, USA
[4]Institute of Materials Research and Engineering, A*STAR, 2 Fusionopolis Way, Innovis, 138634, Singapore

***Abstract* — Although methylammonium lead iodide (MAPI) perovskite solar cells have reached efficiencies above 20%, the material is environmentally unstable. Mixing MAPI with lower dimensional (LD) perovskites has been suggested to improve its stability in recent studies. However, the LD-mixed perovskites have lower device performance, likely as a result of limited charge-carrier mobility due to their decreased structural dimensionality. To understand this effect, we mixed large-*A*-site cation LD perovskites, *tert*-butylammonium lead iodide, with MAPI, and performed a device performance diagnostics. The results suggested although the charge-carrier lifetime was improved, the mobility decreased by a factor of 20. This contributed to a reduction in device efficiency by 2 orders of magnitude, indicating that mobility plays an important role in 3D/LD perovskite mixtures.**

I. Introduction

Organic lead halide perovskites solar cells have reached a record efficiency of 24.2% [1]. However, the most widely studied perovskite, methylammonium lead iodide (MAPI), decomposes into non-perovskite structures, and the degradation process is accelerated in the presence of oxygen, UV radiation, and moisture [2].

To improve environmental stability, MAPI has been mixed with larger *A*-site cations, which forms lower dimensional (LD) perovskites [3]. However, LD perovskite devices perform poorly in comparison to 3D/cubic perovskites [3], [4]. A recent study showed that the LD perovskites with a layered structure have a strong preferred in-plane orientation due to air-liquid interface nucleation [5], suggesting that most charge transport occurs in the in-plane rather than out-of-plane direction since mobility is typically higher in-plane. This is unfavorable for charge extraction in solar cells. In addition, the interplay between the perovskite dimensionality and its solar cell performance is not well understood.

One parameter that determines solar cell performance is charge-carrier diffusion length, which describes the charge-carrier transport dynamics, as shown in Equation 1,

$$L \propto \sqrt{\tau\mu} \qquad (1)$$

where L is the diffusion length, τ is the lifetime, and μ is the mobility. The lifetime of 3D/LD perovskite mixtures is often improved in comparison to the 3D perovskite [6], however the charge-carrier mobility still needs to be understood. Therefore, a deeper look at charge-carrier mobilities in 3D/LD perovskite mixtures will give a better understanding of solar cell performance.

II. Experimental Results

To impose a structural dimensionality change in the perovskite structure, a LD, large-*A*-site cation perovskite, *tert*-butylammonium lead iodide (tBAPI, or T) was mixed with methylammonium lead iodide (MAPI, or M), with known 3D cubic structure [7] in pre-defined volume ratios: 75%:25%, 50%:50%, and 25%:75%. The perovskite was fabricated using a standard procedure [8], with excess PbI_2 (AI : PbI_2 = 1:1.09 for $APbI_3$). T, with a Goldschmidt's tolerance factor of 1.49 (well above the 0.8-1.0 range of cubic perovskite structure [9]), takes a LD structure.

A. Device Performance

A total of 40 devices of these 3D/LD mixtures with standard *n-i-p* architecture [8] were fabricated, with a top electrode of gold, a hole transport layer of Spiro-oMeTAD, an electron transport layer of compact and mesoporous TiO_2, and a bottom electrode of fluorine-doped tin oxide (FTO). The devices were measured under an AM1.5G solar simulator at 1.0 Suns. The data from this measurement was further analyzed by extracting open-circuit voltage (V_{OC}) and short-circuit current (J_{SC}). The results for both V_{OC} and J_{SC}, as well as power conversion efficiency (PCE) are shown in Fig. 1.

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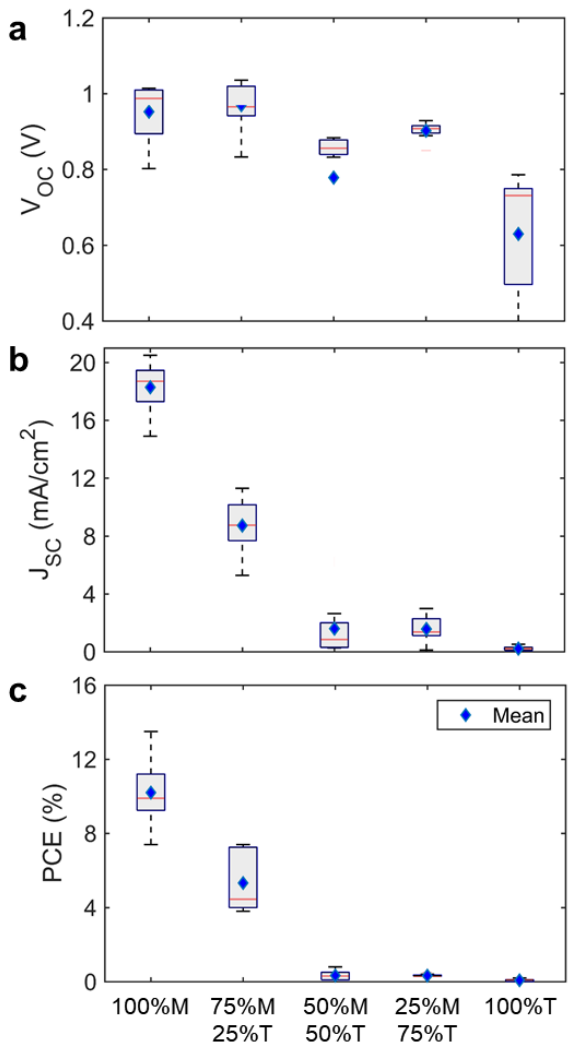

Fig. 1. V_{OC} (a), J_{SC} (b), and PCE (c) of M-T mixtures.

As more T was added into M, J_{SC} was reduced. Although the V_{OC} trend was not apparent, if we consider the increase in bandgap as we added more T into M, the V_{OC} deficit, which is the difference between maximum V_{OC} and measured V_{OC}, actually increased. The combination between the increase of V_{OC} deficit and reduction in J_{SC} led to significant reduction in PCE, since PCE is proportional to both J_{SC} and V_{OC}. The PCE is reduced by 2 orders of magnitude, while the J_{SC} is reduced by 80 times. The fill factor remained approximately constant.

B. Charge-carrier Mobility

Two methods that researchers have tried to understand mobility are time-resolved microwave photo-conductivity (TRMC) [11] and terahertz-probe measurements (THz) [12], [13]. In TRMC measurements, microwaves were used to probe the laser-induced change in conductance of the material, as a function of time [11]. However, to better understand the effect of mobility on M-T mixtures, we conducted THz-probe measurements to investigate the perovskite mobilities in picosecond time scales, as supposed to nanosecond time scales in TRMC. The THz measurements were performed on M-T mixtures, with a wavelength excitation of 400 nm, to include the charge carriers excited from T at lower wavelength. Carrier mobility at different fluences (10-50 μJ cm^{-2}) was calculated from the peak of the conductivity at zero pump-probe delay time, and the result is shown in Table I.

TABLE I
MOBILITY CALCULATED FROM THZ METHOD UNDER 10-50 μJ CM^{-2}

Compounds	Carrier mobility under following fluences (cm^2 V^{-1} s^{-1})		
	12 μJ cm^{-2}	23 μJ cm^{-2}	45 μJ cm^{-2}
100% M	27.77	23.99	20.37
75%M:25%T	25.01	16.51	11.75
50%M:50%T	13.26	9.93	7.34
25%M:75%T	7.06	5.05	3.89
100%T	1.39	1.20	0.71

As fluences were increased, the mobilities of 100%M and the M-T mixtures were reduced. The LD sample (100%T) showed the lowest mobility with respect to the rest of the M-T mixtures, and showed a little fluence dependence in comparison to M-mixed compounds.

C. Charge-carrier lifetime

The charge-carrier lifetime was measured using time-resolved photoluminescence (TRPL) measurement, excited at 532 nm. The biexponential lifetime fitting of the results is shown in Table II.

TABLE II
THE TIME-RESOLVED PHOTOLUMINESCENCE RESULTS FOR M-T SERIES EXCITED AT 532 NM

Mixtures	Biexponential lifetime fitting (ns)
100% M	58
75%M:25%T	98
50%M:50%T	71
25%M:75%T	71

The charge-carrier recombination dynamics showed an improvement as we added T into M, indicated by an increase in lifetime fitting results. Even though the lifetime dropped as we shifted from 75%M:25%T to 50%M:50%T, it still exceeded the 100%M lifetime.

III. DISCUSSION

The PV device performance of M-T perovskite mixtures shows that the combination between the increase of V_{OC} deficit

and J_{SC} results in an efficiency drop. In the future, the bandgap effect should be accounted by calculating the deficit and the normalized parameters instead of comparing the J_{SC} and V_{OC} only.

In general, the reduction in J_{SC} can be affected by device area, surface passivation, reflection, and diffusion length. The device area is controlled by having the same active area defined by a mask for each device measured. The surface passivation also affects the J_{SC} because without passivation, surface recombination at the layer interface increases. We assume that the surface recombination dynamics in M-T mixtures are similar due to similar chemical compositions, hence we can neglect it. J_{SC} is also affected by optical properties, for instance reflection, which needs to be further investigated to decouple its effect on J_{SC}. J_{SC} can also be affected by diffusion length, which is proportional to square root of lifetime and mobility, as shown previously in Equation 1. Even though the lifetime of 3D/LD mixtures is usually improved in comparison to the 3D perovskite [6], which is also shown in TRPL results, it is possible that quantum confinement effects are present in this mixture system, where the 3D perovskite is trapped within LD perovskite regions i.e. phase separation, resulting in long lifetime. Therefore, a deeper study on lifetime of these materials is needed to understand the diffusion length thoroughly.

Besides lifetime, mobility can also affect diffusion length. The mobility reduction in M-T mixtures is shown experimentally in THz measurements, for different fluences. Generally, the trend of reduction in mobility from M to T and from low to high fluences is present. This deviation could be due to carrier-carrier scattering effects. The LD perovskite, however, is less affected by the fluence level. THz measurements show that mobility reduction is an important factor in performance reduction of 3D/LD perovskite mixtures.

IV. Summary

In this study, 3D/LD perovskite mixtures were fabricated, and their device performance and mobility were studied. The addition of LD perovskite (T) into 3D perovskite (M) induced structural dimensionality change and solar device performance. The addition of as little as 25% T led to increase of V_{OC} deficit and decrease of J_{SC} , which reduced the overall efficiency. The charge-carrier mobility, affected by large amounts of LD perovskites, also decreased. The reduction of mobility by a factor of 20 contributed to 2 orders of magnitude reduction of efficiency. This effect must be considered when developing these types of mixtures for stability improvement purposes in perovskite solar cells.

Author Information

Juan-Pablo Correa-Baena is now at Georgia Institute of Technology.

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