

HYSTERESIS-FREE PEROVSKITE SOLAR CELLS MADE OF POTASSIUM-DOPED ORGANOMETAL HALIDE PEROVSKITE

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Organometal halide perovskites have captured wide interest as a promising material for low-cost and high-efficiency solar cells. The power conversion efficiency (PCE) of the organometal halide perovskite solar cells (PSCs) has reached 22% within a few years of its advent, which is comparable to those of polycrystalline Si solar cells (21.9%), CdTe solar cells (22.1%), and CIGS solar cells (22.6%). Through recent studies of PSCs, the composition of organometal halide perovskites is recognised as one of the key factors in the improvement of the PCE. As for the organic cation methylammonium (MA), the mixing of formamidinium (FA) extended the absorption edge from 800 nm to 850 nm, and then the photocurrent of PSC was enhanced. However, the pure formamidinium lead iodide (FAPbI₃) contained the non-perovskite phase (δ -phase), which resulted in the low PCE of the perovskite solar cells. To suppress the creation of the δ -phase, the methylammonium chloride or bromide (MACl or MABr, respectively) was incorporated into the perovskite layer, and the PCE was improved to more than 20%. It was also verified that the incorporation of caesium cations (Cs⁺) into the A-site of perovskite inhibited the creation of the δ -phase, which considerably promoted the stability of the perovskite phase and the reproducibility of PSCs. Recently, it was reported that the incorporation of rubidium cations (Rb⁺) into the A-site of the perovskite promoted the PCE to more than 21%, although the ionic radius of Rb⁺ (148 pm) was smaller than that of Cs⁺ (169 pm) and, according to the Goldschmidt's tolerance factor, the formation of a stable perovskite structure was considered to be difficult. The above findings motivated us to investigate potassium cations (K⁺) with an ionic radius (133 pm) for improving the photovoltaic performance of PSCs. Potassium is abundant in the earth's crust (21, 000 ppm), as compared to caesium (90 ppm) or rubidium (3 ppm), and it is available cheaply.

On the other hand, there is a big issue with I-V hysteresis of PSCs that causes uncertainty as to its real PCE. Several hypotheses, such as ion migration, polarisation, defect traps, and capacitance, have been discussed to explain I-V hysteresis. In the conventional structure of PSCs, the difference of the conduction band edge between the TiO₂ and the perovskite forms a small barrier at the interface, which retards the transportation of electrons from the perovskite to the TiO₂. As for the electron transport layer (ETL), when TiO₂ with a relatively higher conduction band minimum (CBM) was replaced by SnO₂ or Cl-capped TiO₂ with relatively lower CBM, the I-V hysteresis was diminished, indicating the disappearance of the electron transfer barrier. These results suggested that the band engineering of the organometal halide perovskite by composition tuning is important for diminishing I-V hysteresis.

In this study, we explored the feasibility of incorporating K⁺ into the perovskite absorber. The results revealed that incorporating a small amount of K⁺ into the double organic cation perovskite absorber (FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})₃) improved the photovoltaic performance of PSCs significantly, and K⁺ incorporation diminished I-V hysteresis. The potassium-doped organometal halide perovskite solar cells (PSCs) of more than 20% power conversion efficiency (PCE) without I-V hysteresis were constructed. To understand the mechanism of the phenomena, we investigated the influence under various K⁺ ratios in the perovskite absorber. The crystal lattice of the organometal halide perovskite was expanded with increasing of the potassium ratio, where both absorption and photoluminescence spectra shifted to the longer wavelength, suggesting that the optical band gap decreased. In the case of the perovskite with the 5% K⁺, the conduction band minimum (CBM) became similar to the CBM level of the TiO₂-Li. In this situation, the electron transfer barrier at the interface between TiO₂-Li and the perovskite was minimised. In fact, the transient current rise at the maximum power voltages of PSCs with 5% K⁺ was faster than that without K⁺. It is concluded that stagnation-less carrier transportation could minimise the I-V hysteresis of PSCs.