Effects of copper addition to methylammonium/potassium-based perovskite solar cells

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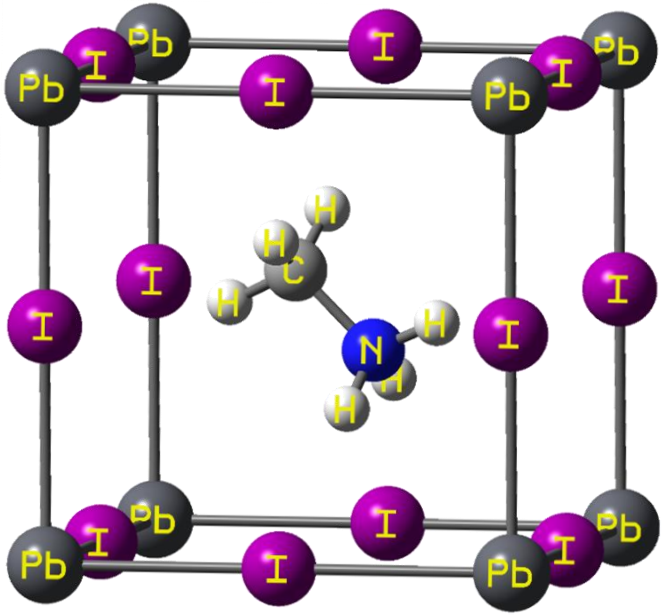
$MAPbI_3$ perovskite solar cells

Advantages
- Low fabrication cost
- Highly sensitive to visible light

Actively researched worldwide

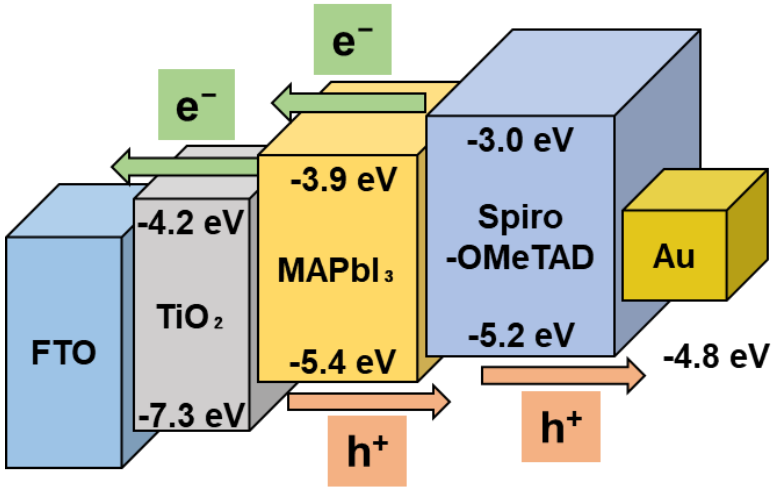


$CH_3NH_3PbI_3$ perovskite crystal

$CH_3NH_3 = MA$

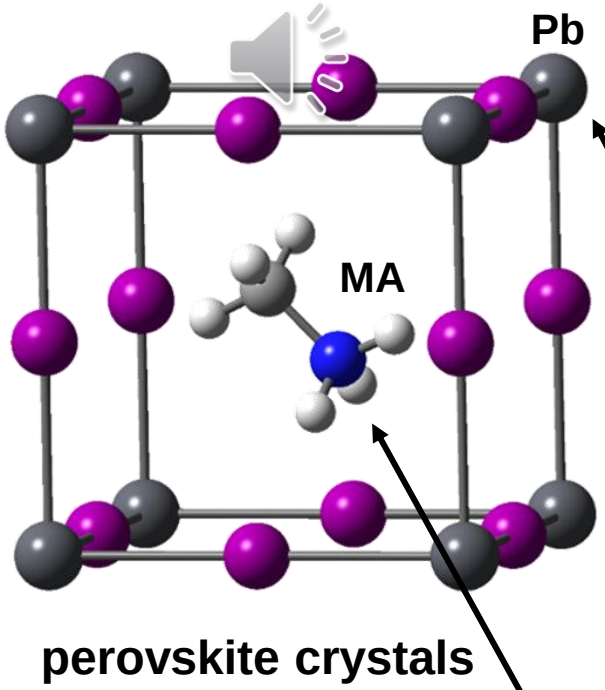
Serious problems
- Low durability
- Toxicity of lead (Pb)

Introduction of additives into perovskite crystals



Energy level diagram

Improvement methods



Cu：Low toxicity, Alternative candidate of Pb

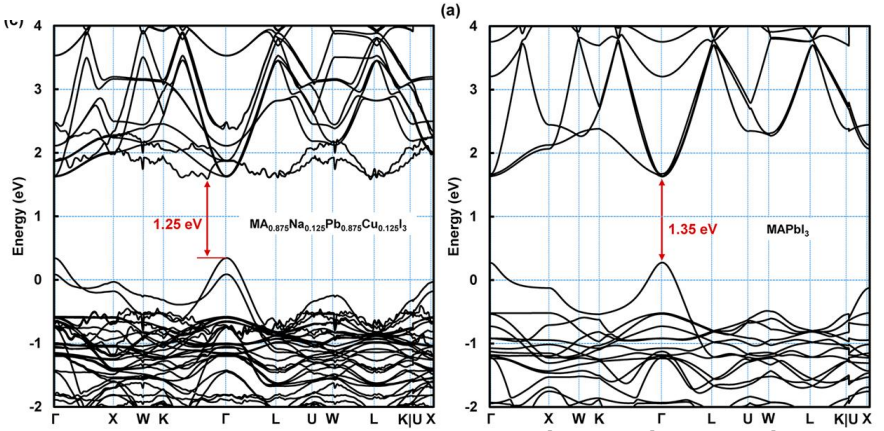
Water-quality standards; Pb : 0.01 mg/L Cu : 1.0 mg/L

Ministry of Health, Labor and Welfare

M. T. Klug, et al , Energy Environ. Sci., 10, 236 (2017).

：Narrow energy gap E_g, Light effective mass

→ Improved career mobility



N. Ueoka, et al, *RSC Adv. 9*, 24231, (2019).

K：Alkali metals at the MA sites

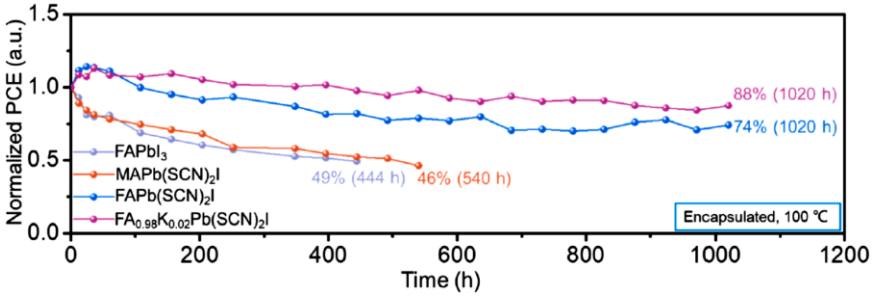
⇒ Candidate for substitution

：Abundance in the earth's crust

K (21,000 ppm) Cs (90 ppm), Rb (3 ppm)

⇒Low cost

： Long-term stability Z. Tang, et al. Sci. Rep.12183 (2017).



Y. Xia, et al. Nat, J. of Power Sources, 494, 229781, (2021).

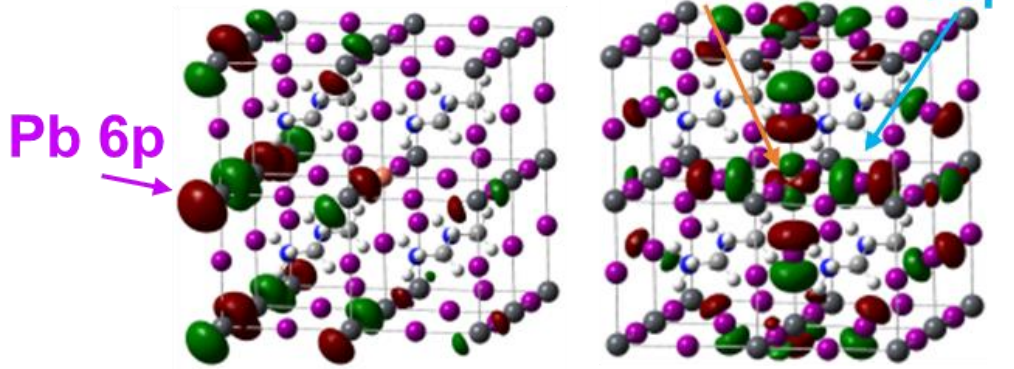
Objective

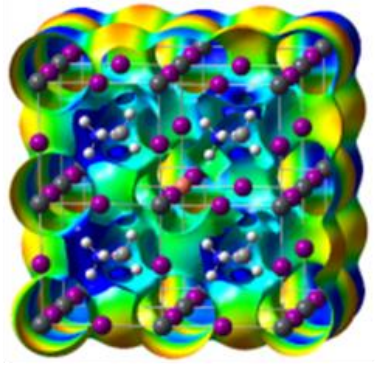
Perovskite solar cells doped with Cu and K were fabricated and characterized. Additive effects on the photovoltaic properties were investigated by experimental results and calculation on the electronic structures and thermodynamic stability.

Electronic structures at HOMO and LUMO & ESP

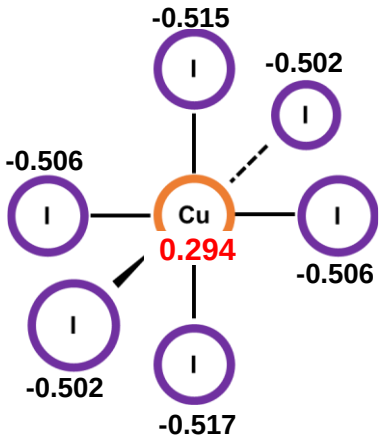
Partial charge

$MAPb_{0.963}Cu_{0.037}I_3$





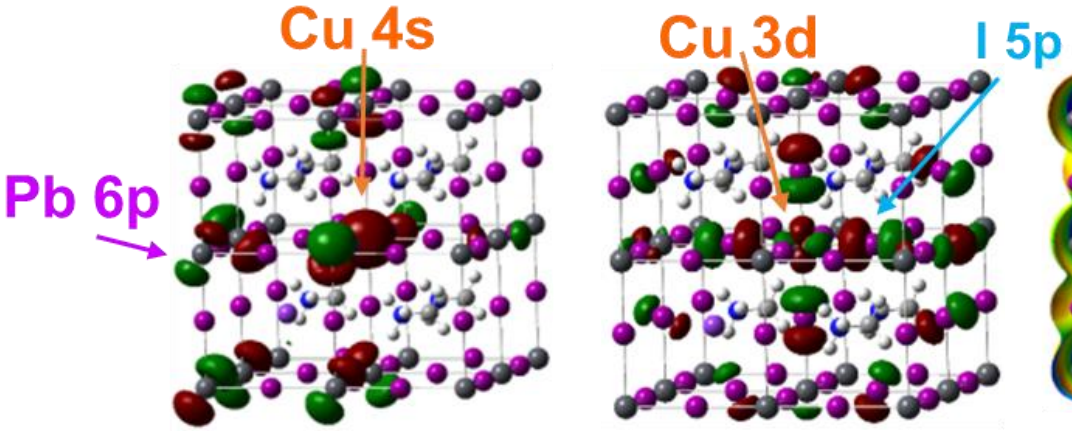
Electrostatic potential

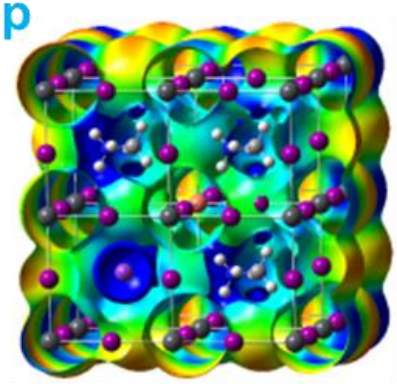


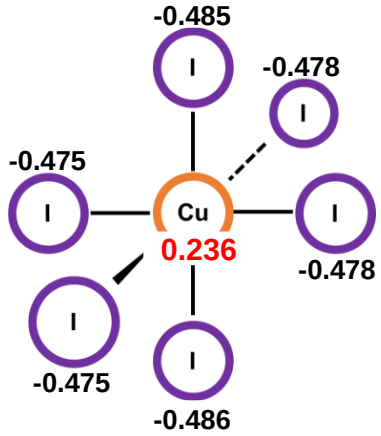
LUMO: Pb 6p, HOMO: I 5p, Cu 3d

Promotion of charge transfer
→ Improved carrier mobility

$MA_{0.875}K_{0.125}Pb_{0.963}Cu_{0.037}I_3$







LUMO: Pb 6p, Cu 4s, HOMO: I 5p, Cu 3d
➡Change of transition state

ESP: Delocalization
➡ Estimate of J_{SC} increase

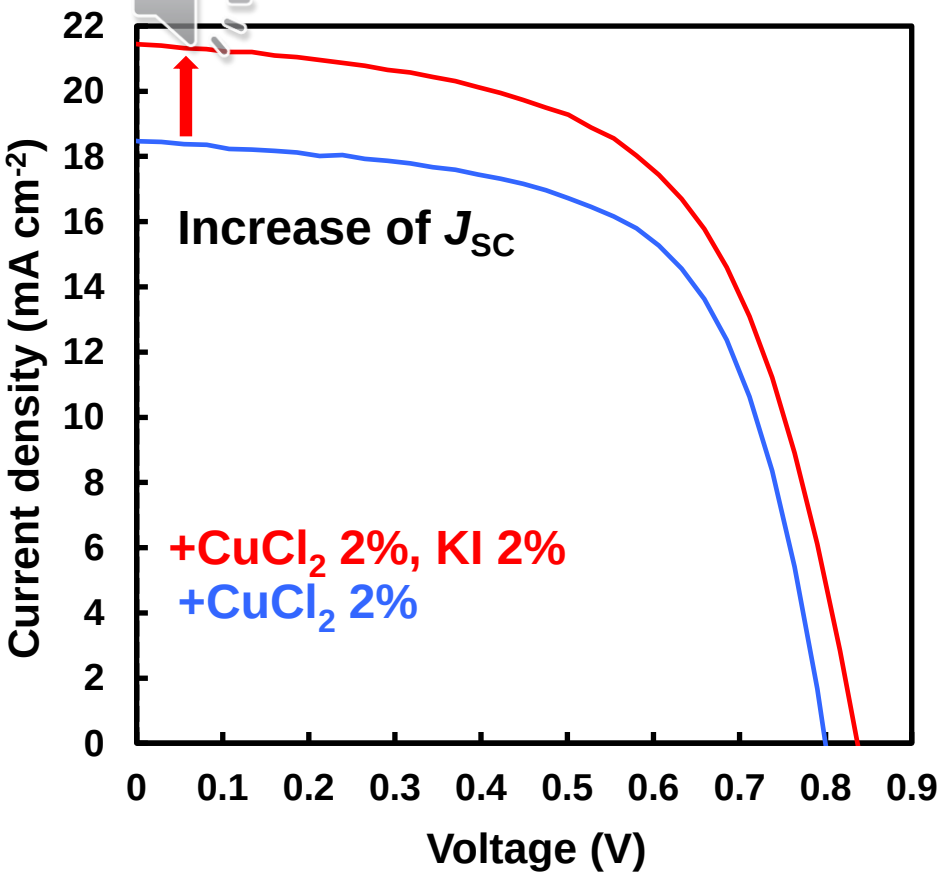
Calculation condition by Gaussian
$MAPb(Cu)I_3$, $MA(K)Pb(Cu)I_3$: B3LYP, LANL2MB
2 × 2 × 2 cell, cubic

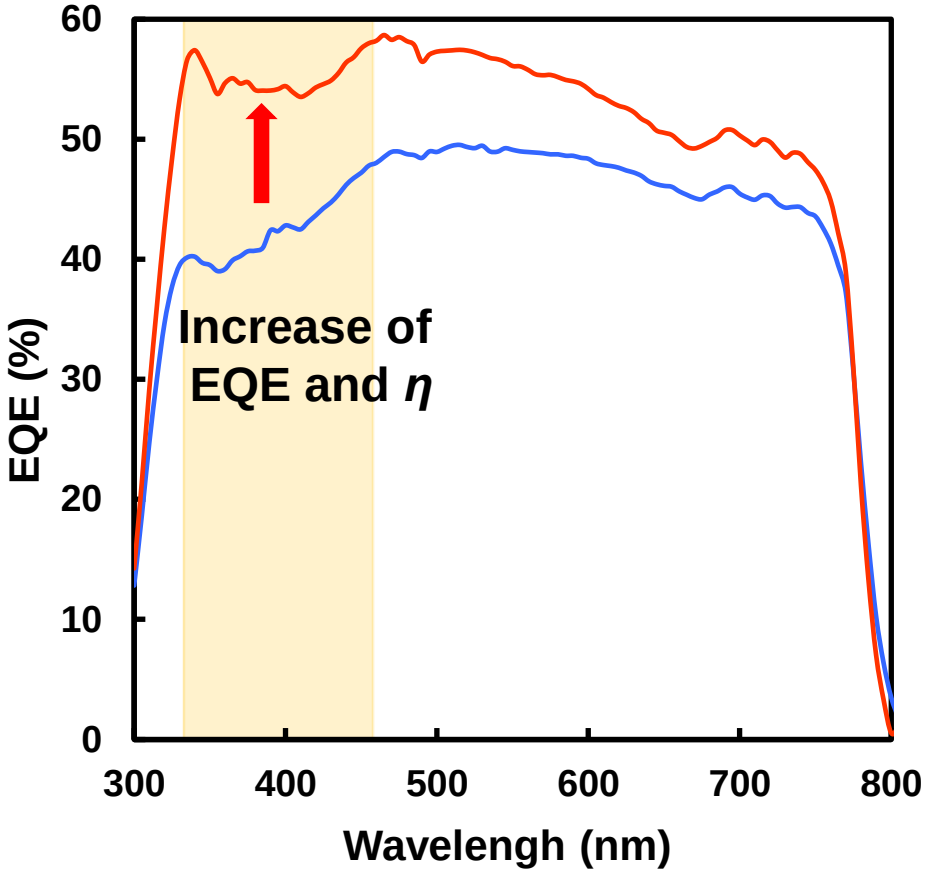
I N C Pb Cu H

9.52 eV 13.6 eV

$$J_P = (q \cdot p \cdot \nu) - J_{DP}$$

J-V characteristics and EQE spectra





Devices	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)	η_{ave} (%)	E_g (eV)
+Cu 2%	18.5	0.800	0.627	9.26	8.47	1.56
+Cu 2%, K 2%	21.4	0.837	0.590	10.59	8.99	1.56

Stability of conversion efficiencies

After 28 days

Devices	J_{SC} (mA cm^{-2})	V_{OC} (V)	change of η (%)
+$CuCl_2$ 2%	18.5 ➡ 16.9	0.800 ➡ 0.785	-15.3
+$CuCl_2$ 2%, KI 2%	21.4 ➡ 18.6	0.837 ➡ 0.880	1.47

Preservation of efficiency after 28 days ⇒ Long-term stability

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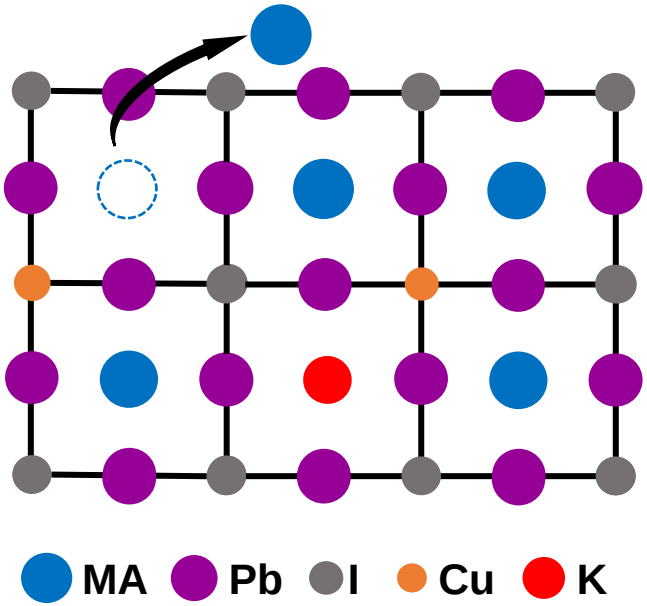
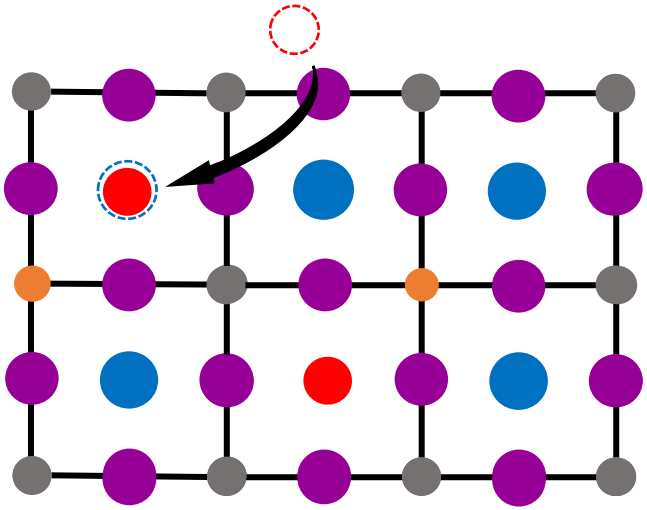
MA desorption with time



K^+ existing at the grain boundaries
➡ Occupation at the MA vacancy



Long-term stabilization by suppressing decomposition of perovskite crystals

Conclusion

Effects of co-addition of Cu/K to $MAPbI_3$

- **Charge delocalization promotes carrier transfer.**
  ⇒Improvement of J_{SC} and η of devices

- **Long-term stabilization by suppressing decomposition of perovskite crystals**