Effects of halogens and alkali metals on guanidinium/ethylammonium doped perovskite photovoltaic devices

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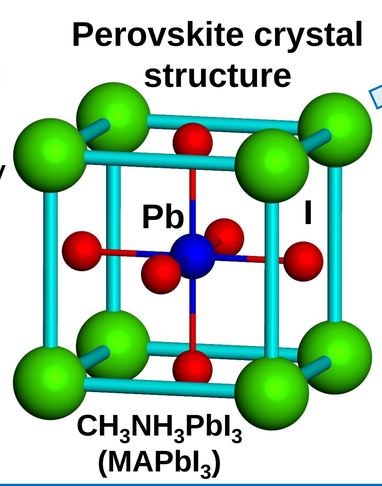
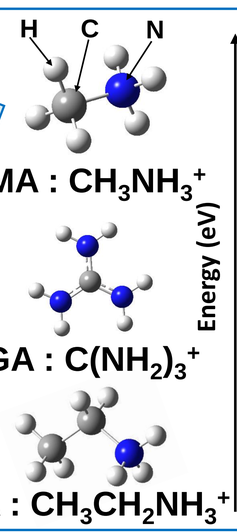
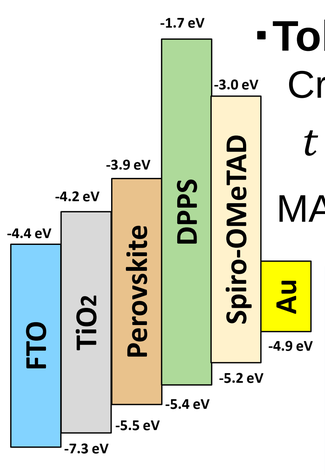
Introduction

Perovskite solar cell

- **Advantage**
  - Inexpensive and easy
  - High efficiency
  - Wide variety
- **Problem**
  - Low stability
  - large cell







- **Tolerance factor *t***

Crystal structure strain and stability indicators.

$$t = \frac{r_A + r_x}{\sqrt{2}(r_B + r_x)} \quad r: \text{Ion radius of each site}$$

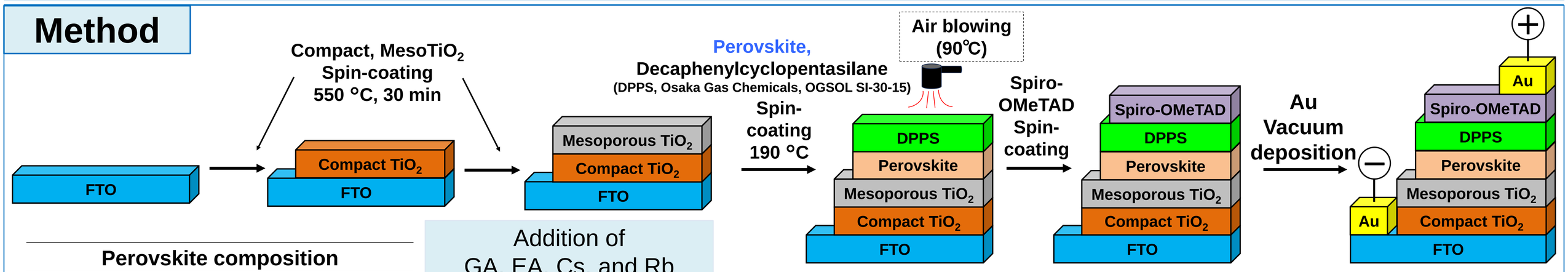
$MAPbI_3$: 0.911 → Made this time : 0.920~0.924

A Site	B Site
MA : 2.17 Å	Pb : 1.19 Å
GA : 2.78 Å	X Site
EA : 2.74 Å	I : 2.20 Å
Rb : 1.72 Å	Br : 1.96 Å
Cs : 1.88 Å	Cl : 1.81 Å

Purpose

- **Improved power generation efficiency and durability.**
- **Fabrication and characterization of Perovskite solar cells with diverse compositions.**

Method

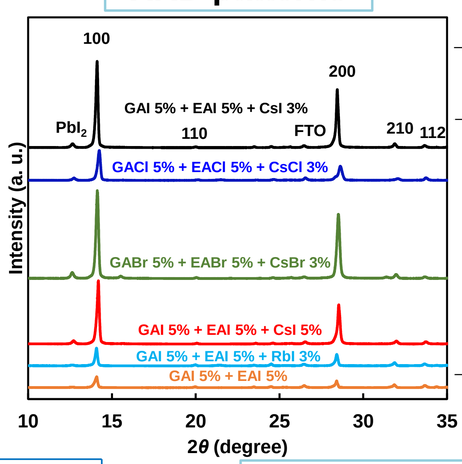


Perovskite composition

① $MA_{0.87}GA_{0.05}EA_{0.05}Cs_{0.03}PbI_3$
② $MA_{0.87}GA_{0.05}EA_{0.05}Cs_{0.03}PbI_{2.87}Br_{0.13}$
③ $MA_{0.87}GA_{0.05}EA_{0.05}Cs_{0.03}PbI_{2.95}Br_{0.05}$
④ $MA_{0.87}GA_{0.05}EA_{0.05}Cs_{0.03}PbI_{2.95}Cl_{0.13}$
⑤ $MA_{0.90}GA_{0.05}EA_{0.05}PbI_3$
⑥ $MA_{0.87}GA_{0.05}EA_{0.05}Rb_{0.03}PbI_3$
⑦ $MA_{0.85}GA_{0.05}EA_{0.05}Cs_{0.05}PbI_3$

Addition of GA, EA, Cs, and Rb
→ A Site Composition Varying additive halogens
→ Expected to improve **conversion efficiency** and **stability**

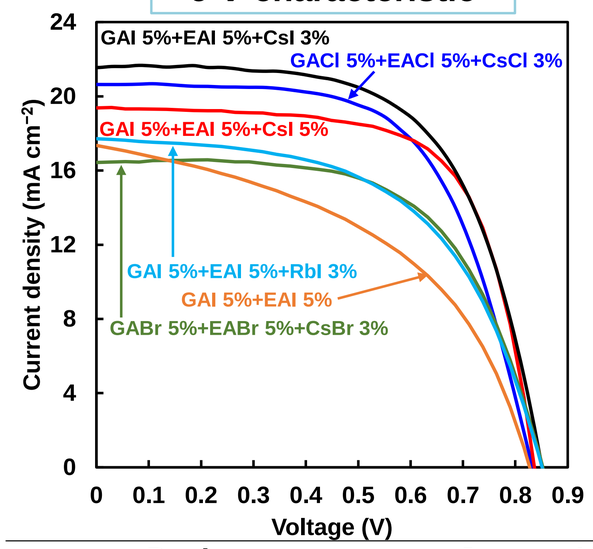
XRD patterns



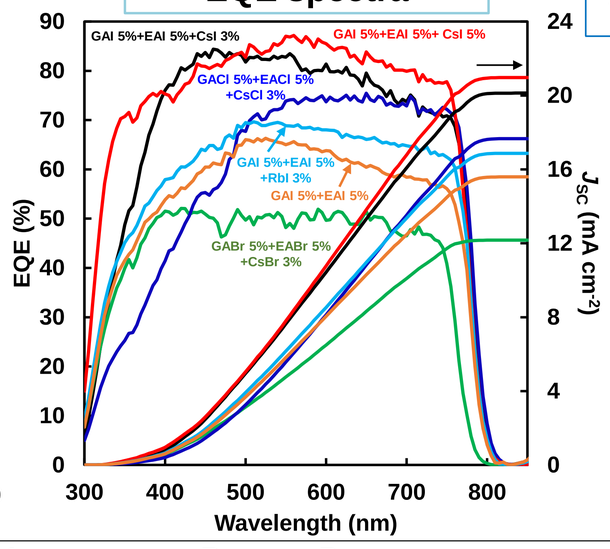
Devices Additive (%)	Lattice constant (Å)	Crystallite size *D* (Å)	I_{100} / I_{210}
GAI 5 + EAI 5	6.279(2)	587	3.28
GAI 5 + EAI 5 + CsI 3	6.268(0)	641	19.3
GACl 5 + EACl 5 + CsCl 3	6.252(0)	470	13.0
GABr 5 + EABr 5 + CsBr 3	6.257(2)	498	19.1
GAI 5 + EABr 5 + CsI 3	6.272(0)	568	9.0
GAI 5 + EAI 5 + CsI 5	6.265(1)	617	18.8
GAI 5 + EAI 5 + RbI 3	6.278(1)	504	5.01

Results

J-V characteristic

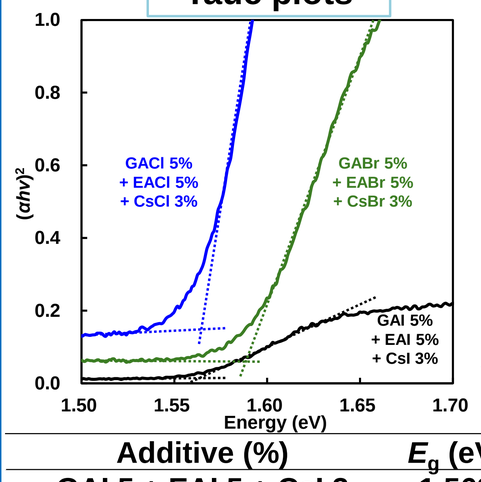


EQE spectra



Devices Additive (%)	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF*	R_S (Ω cm^2)	R_{Sh} (Ω cm^2)	η (%)	η_{ave} (%)	E_g (eV)
GAI 5 + EAI 5	17.4	0.828	0.467	7.17	176	6.71	5.76	1.55
GAI 5 + EAI 5 + CsI 3	21.6	0.850	0.621	4.81	3828	11.4	10.4	1.55
GACl 5 + EACl 5 + CsCl 3	20.6	0.833	0.619	8.28	7388	10.6	9.35	1.55
GABr 5 + EABr 5 + CsBr 3	16.4	0.852	0.610	6.82	2329	8.55	7.54	1.59
GAI 5 + EABr 5 + CsI 3	13.4	0.697	0.597	4.46	1420	5.60	3.51	1.55
GAI 5 + EAI 5 + CsI 5	19.4	0.837	0.672	2.58	1366	10.9	8.78	1.55
GAI 5 + EAI 5 + RbI 3	17.7	0.851	0.555	8.49	606	8.36	6.41	1.55

Tauc plots



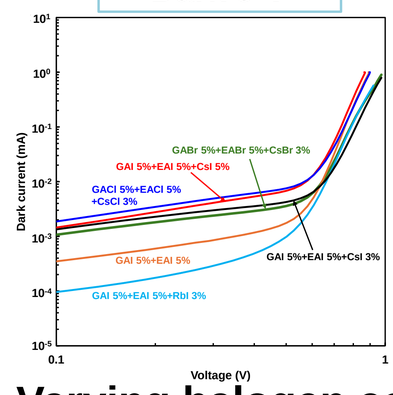
Additive (%)	E_g (eV)
GAI 5 + EAI 5 + CsI 3	1.563
GACl 5 + EACl 5 + CsCl 3	1.565
GABr 5 + EABr 5 + CsBr 3	1.588

Devices Additive (%)	Time (Days)	η (%)	η_{ave} (%)	Rate of change (% Day^{-1})
GAI 5 + EAI 5	98	8.21	6.83	+0.229
GAI 5 + EAI 5 + CsI 3	100	9.34	8.16	-0.180
GACl 5 + EACl 5 + CsCl 3	100	9.36	8.31	-0.120
GABr 5 + EABr 5 + CsBr 3	100	7.82	6.82	-0.0846
GAI 5 + EABr 5 + CsI 3	98	3.02	2.27	-0.470
GAI 5 + EAI 5 + CsI 5	100	9.36	8.26	-0.141
GAI 5 + EAI 5 + RbI 3	98	6.96	6.27	-0.171

- η rate of change (additive halogen)
  Br > I > Cl

Br used at X site : effective for stability

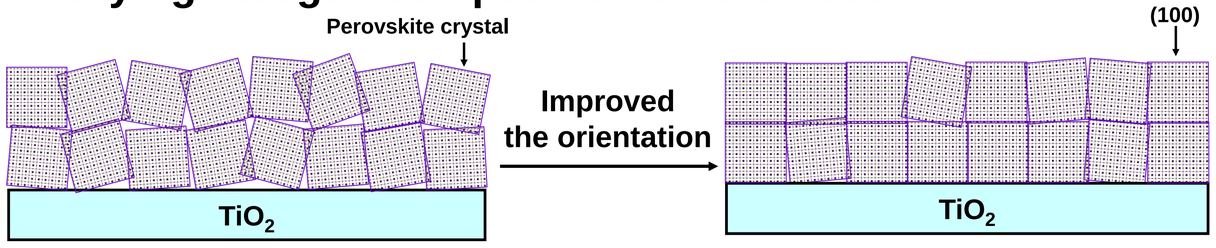
Dark *J-V*



Devices Additive (%)	V_{TFL} (V)	Trap Density (×10^{15} cm^{-3})
GAI 5 + EAI 5	0.57	8.4
GAI 5 + EAI 5 + CsI 3	0.53	7.8
GACl 5 + EACl 5 + CsCl 3	0.54	8.0
GABr 5 + EABr 5 + CsBr 3	0.58	8.6
GAI 5 + EABr 5 + CsI 3	0.55	8.1
GAI 5 + EAI 5 + CsI 5	0.51	7.6
GAI 5 + EAI 5 + RbI 3	0.51	7.6

$$N_t = \frac{2V_{TFL}\varepsilon_0\varepsilon}{eL^2} \quad V_{TFL}: \text{Trap fill limit voltage}$$

- **Varying halogen composition of additives**

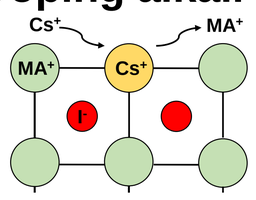


- Improved orientation → decreased grain boundary

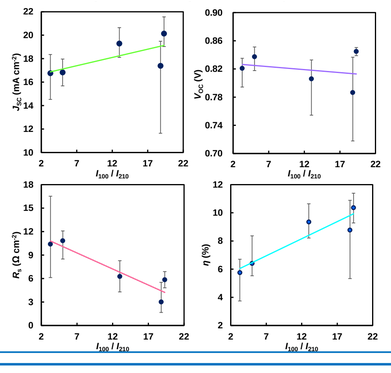
(Scattering of electrons by grain boundaries → electrical resistance(R_S))

$$\eta_n = J_{SC}V_{OC}FF \ , \ I = I_{SC} - I_0\left[\exp\left\{\frac{q(V+R_SI)}{nkT}\right\} - 1\right] - \frac{V+R_SI}{R_{Sh}}$$

- **Doping alkali metal cations to A site**



- Metal ion doped → high conversion efficiency
  ⇒ Desorption ease : MA^+ > Metal cation (Cs^+, Rb^+)
  ⇒ <u>**Stabilization of structure**</u>



- **Improved structural stability and orientation**
  → <u>Improved short-circuit current density and conversion efficiency</u>
- Cs^+, Rb^+ 3% addition → V_{OC} improvement (introduced at defects and grain boundaries)

Conclusion

Reference: H. Shimada, T. Oku, I. Ono, R. Okumura, K. Kuroyanagi, A. Suzuki, T. Tachikawa, T. Hasegawa, S. Fukunishi, Hybrid Advances 6 (2024) 100252.

- **Changed halogen composition of additives**
  → ・Effects of halogen : I > Cl > Br
  ・Addition of Br : stability, E_g increase is affected.
- **Addition of Alkali metal cations to A site**
  → ・Effects of ions added in addition to GA / EA : Cs^+ > Rb^+ > none
  (∵ Ease of detachment : MA^+ > Alkali metal cations (Cs^+, Rb^+))
  ・Cs addition : 3% is considered more appropriate.