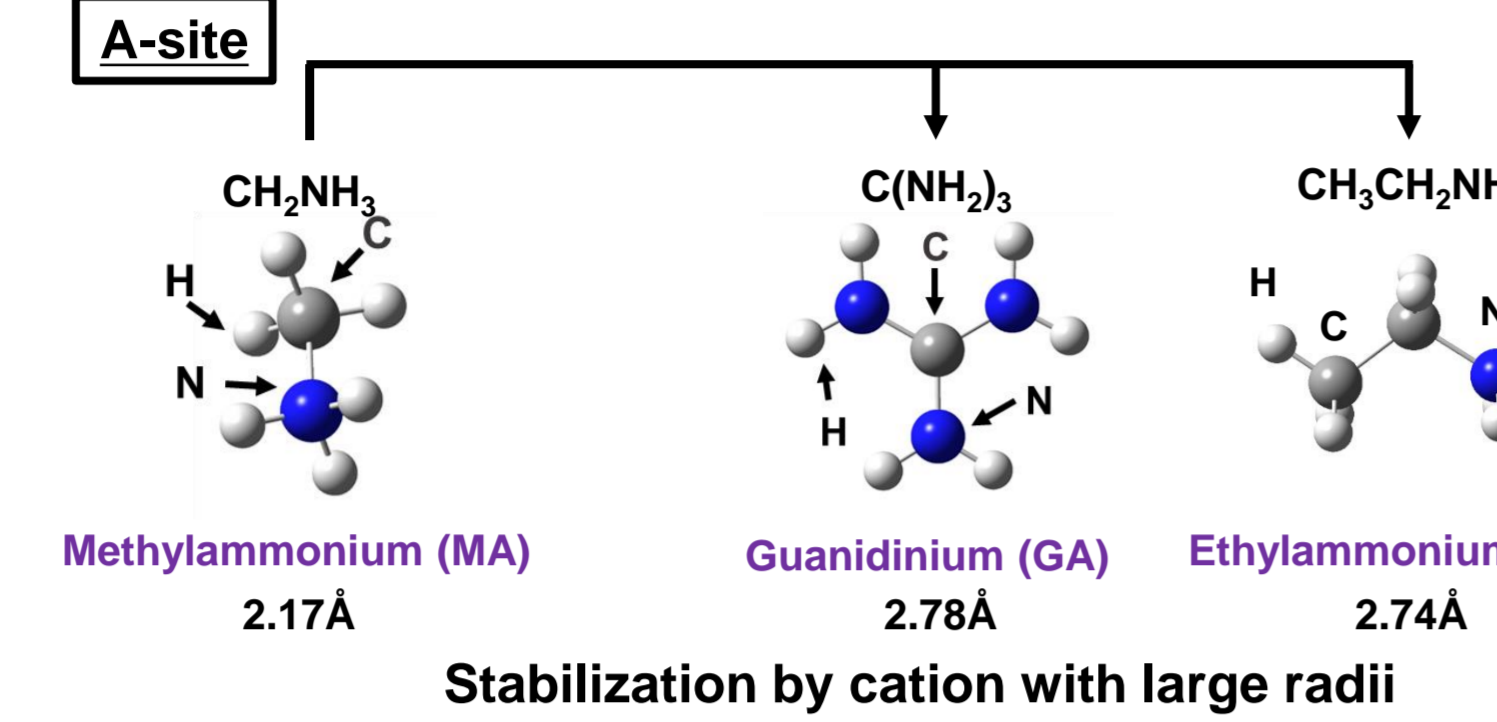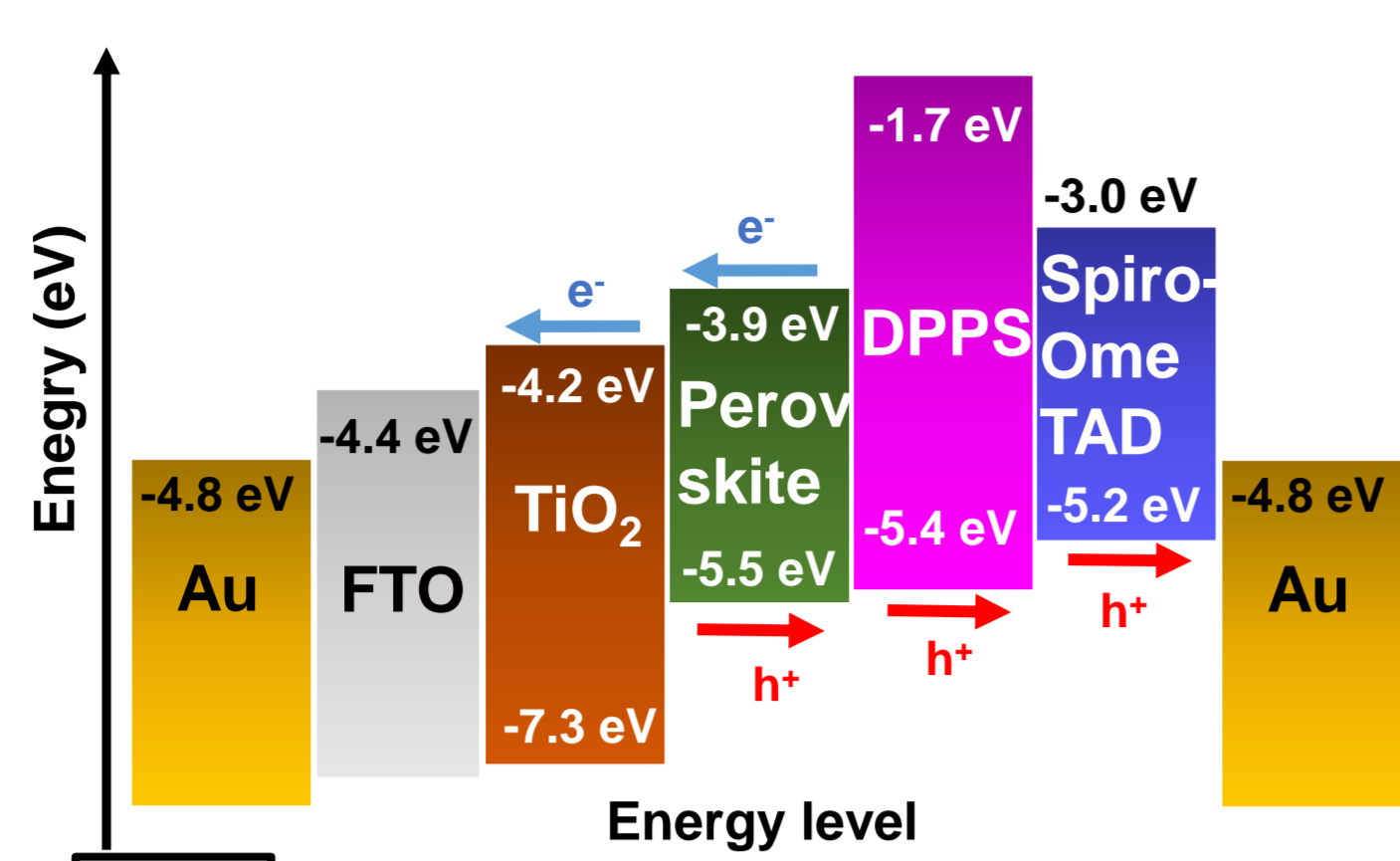# Fabrication and characterization of GA-, EA-, and Rb-added perovskite solar cells passivated with DPPS

Takeo Oku[1], Iori Ono[1], Keisuke Kuroyanagi[1], Atsushi Suzuki[1], Tomoharu Tachikawa[2], Tomoya Hasegawa[2], and Sakiko Fukunishi[2]

[1]Department of Materials Science, The University of Shiga Prefecture, Japan   [2]Osaka Gas Chemicals Co., Ltd., Japan

Contact information: oku@mat.usp.ac.jp

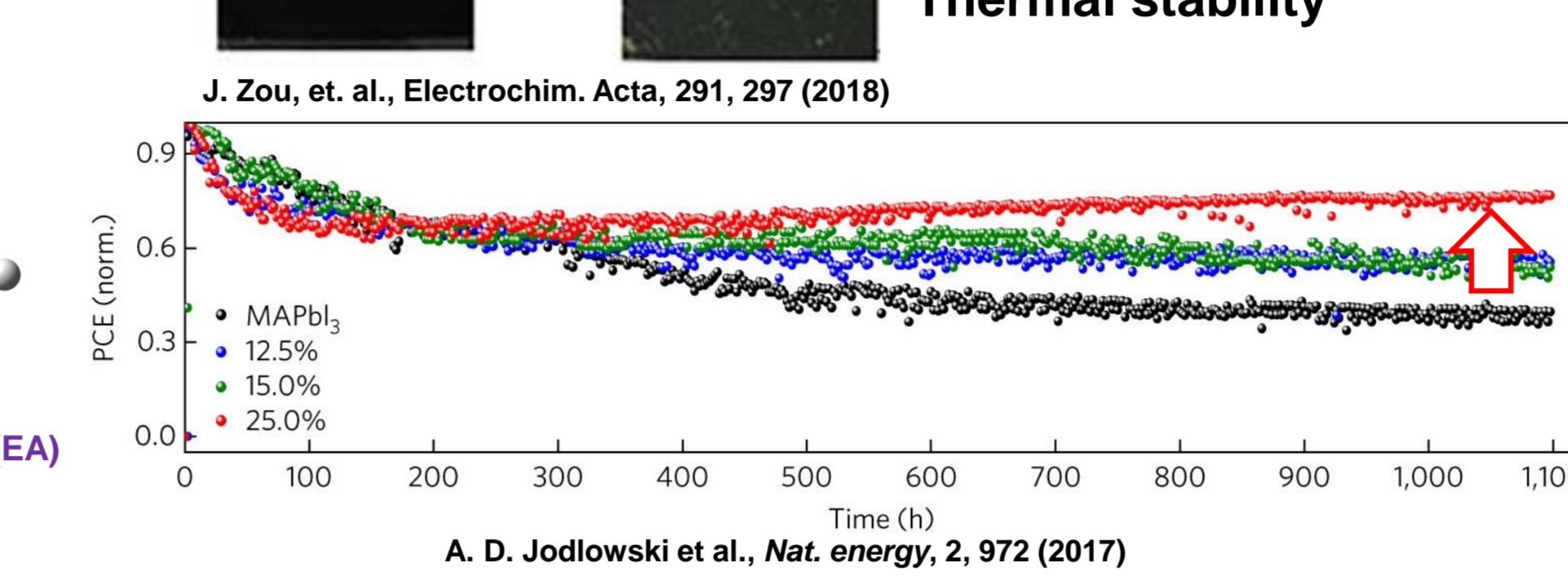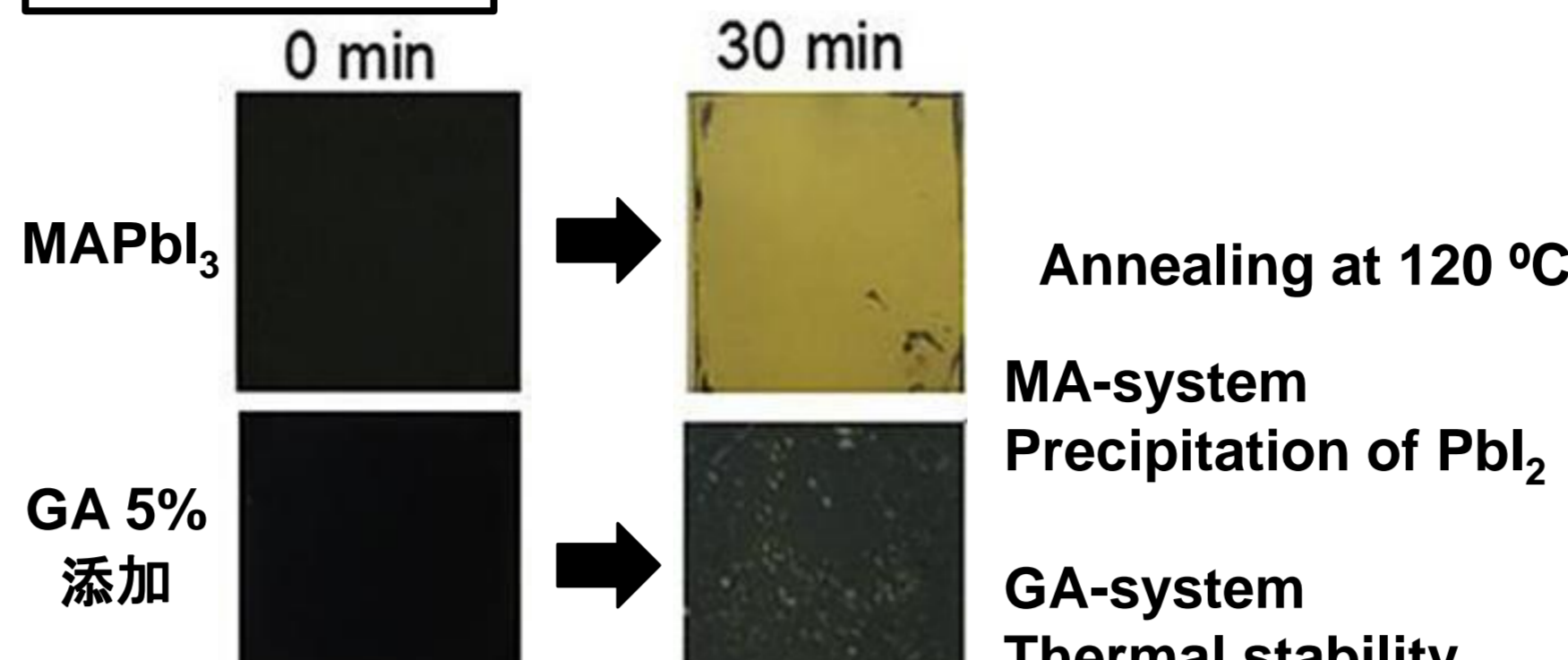THE UNIVERSITY OF SHIGA PREFECTURE   OSAKA GAS CHEMICALS

References
I. Ono, T. Oku, A. Suzuki, S. Fukunishi, T. Tachikawa, and T. Hasegawa, Materials Today Communications 38 (2024) 107623.
K. Kuroyanagi, T. Oku, I. Ono, R. Okumura, A. Enomoto, A. Suzuki, S. Fukunishi, T. Tachikawa, T. Hasegawa, Nano Trends 5 (2024) 100030.
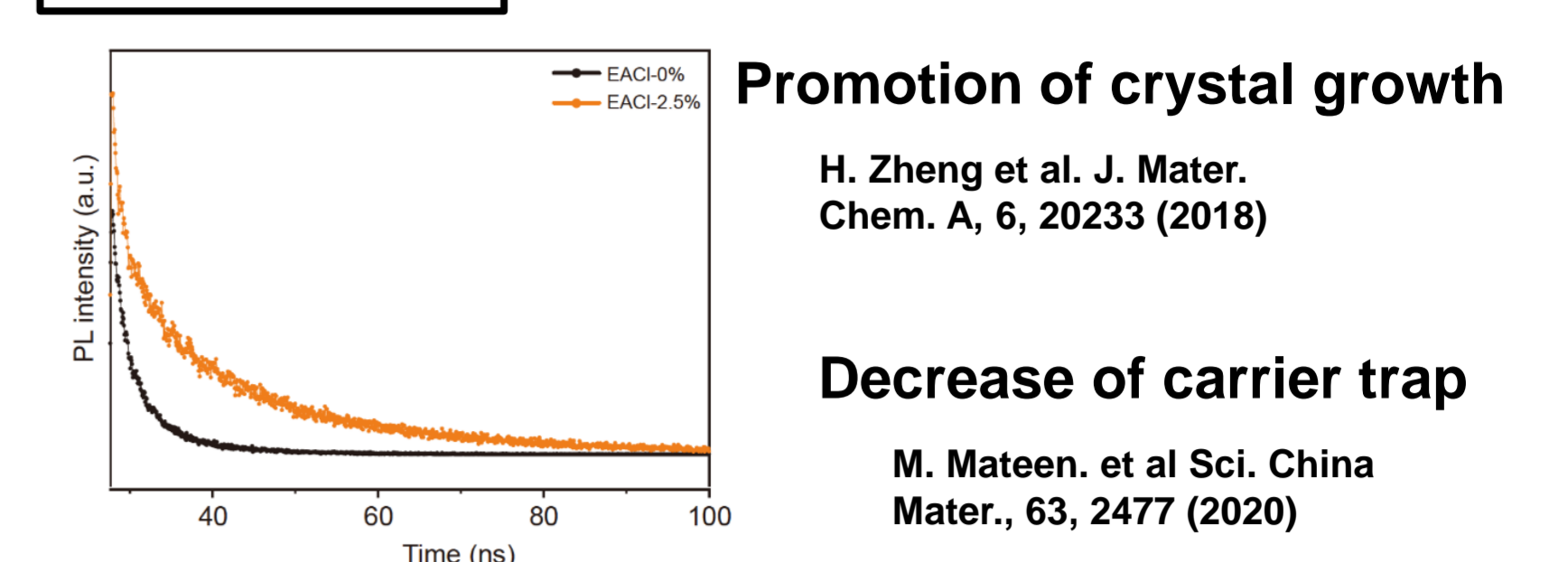
Introduction

CH₃NH₃ (MA)

Perovskite solar cells
- High efficiencies
- Easy fabrication process
- Possible application for IoT
- Desorption of CH₃NH₃ (MA) → Instability

A-site:
- Methylammonium (MA) 2.17Å
- Guanidinium (GA) 2.78Å
- Ethylammonium (EA) 2.74Å

Stabilization by cation with large radii

GA addition

MAPbI₃ — Annealing at 120 °C — MA-system: Precipitation of PbI₂
GA 5% 添加 — GA-system: Thermal stability

J. Zou, et. al., Electrochim. Acta, 291, 297 (2018)

A. D. Jodlowski et al., *Nat. energy*, 2, 972 (2017)

EA addition

Promotion of crystal growth
H. Zheng et al. J. Mater. Chem. A, 6, 20233 (2018)

Decrease of carrier trap
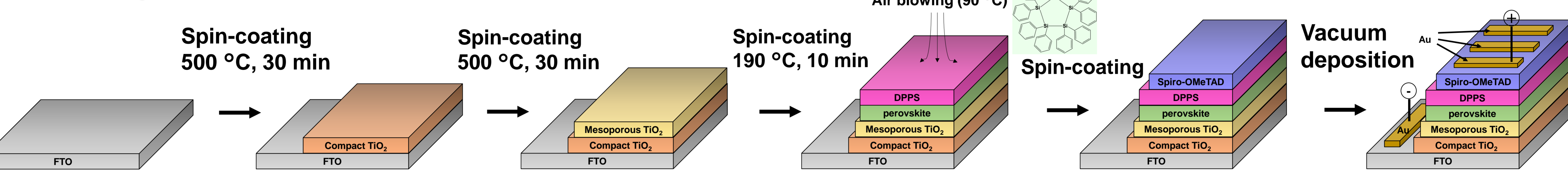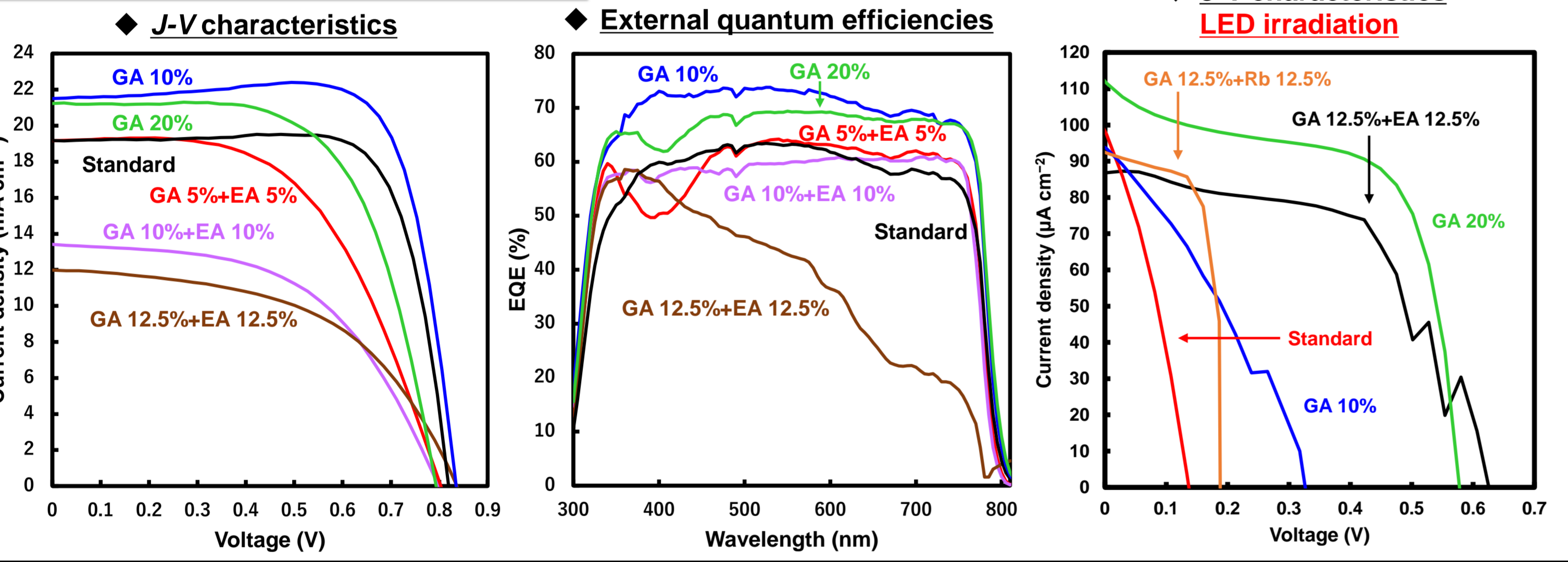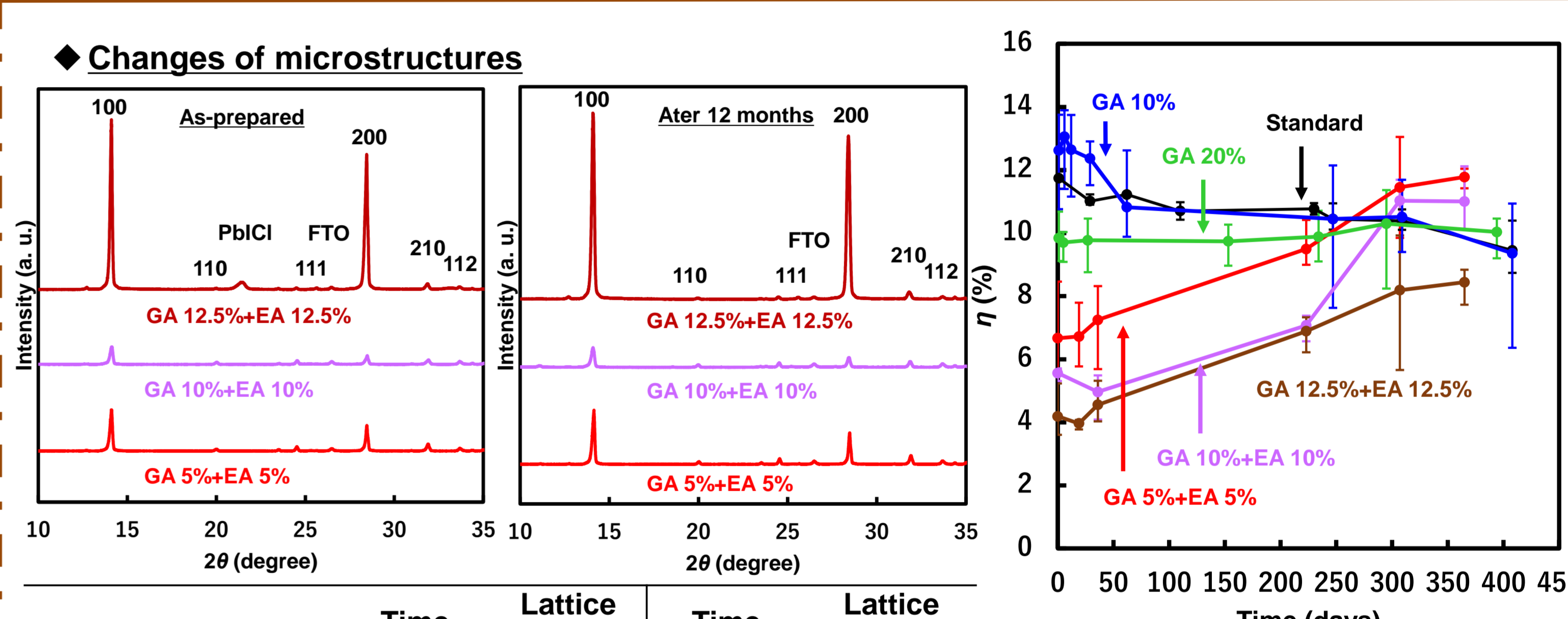M. Mateen. et al Sci. China Mater., 63, 2477 (2020)

Purpose

- Fabrication of EA or Rb added GA-based MAPbI₃ solar cells.
- Evaluation by experiments and calculation.
- Characteristics under LED.

Fabrication process

Spin-coating 500 °C, 30 min → Spin-coating 500 °C, 30 min → Spin-coating 190 °C, 10 min → Air blowing (90 °C) → Spin-coating → Vacuum deposition

Decaphenylcyclopentasilane (DPPS, Osaka Gas Chemicals, OGSOL SI-30-15)

Results and Discussion

◆ J-V characteristics

◆ External quantum efficiencies

◆ J-V characteristics LED irradiation

Devices	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	R_S (Ω cm²)	R_{Sh} (Ω cm²)	η (%)	η_{ave} (%)	E_g (eV)
Standard	19.2	0.819	0.760	4.78	635	11.9	11.7	1.55
GA 10%	21.3	0.835	0.773	4.66	633	13.9	13.2	1.53
GA 20%	21.2	0.793	0.634	7.64	238	10.7	9.84	1.55
GA 5%+EA 5%	19.2	0.803	0.550	13.3	5050	8.46	6.69	1.57
GA 10%+EA 10%	13.4	0.798	0.533	14.8	704	5.71	3.87	1.57
GA 12.5%+ EA 12.5%	12.0	0.836	0.522	12.1	869	5.23	3.91	1.58
Standard (LED)	0.113	0.136	0.329	4.97	3.17×10³	1.47	1.40	—
GA 10% (LED)	0.108	0.326	0.574	3.55	8.60×10³	4.87	2.41	—
GA 20% (LED)	0.129	0.578	0.615	8.67	4.17×10⁴	13.3	10.4	—
GA 12.5%+EA 12.5% (LED)	0.100	0.626	0.574	34.4	1.89×10⁵	10.4	6.52	—

◆ X-ray diffraction

Devices	Lattice constant (Å)	I_{100}/I_{210}
Standard	6.268(0)	2.66
GA 10%	6.276(1)	3.64
GA 20%	6.278(1)	2.01
GA 5%+EA 5%	6.268(0)	5.47
GA 10%+EA 10%	6.264(0)	3.48
GA 12.5%+EA 12.5%	6.270(0)	25.7

Increase of lattice constants → Introduction of GA and EA

◆ First-principles calculation

Devices	Total energy (eV cell^{-1})	m_e^*/m_0	m_h^*/m_0	VBM (eV)	CBM (eV)
MAPbI₃	-3496	0.59	0.33	0.283	1.61
MA₀.₇₅GA₀.₂₅PbI₃	-3629	1.49	0.31	0.203	1.52
MA₀.₇₅GA₀.₁₂₅EA₀.₁₂₅PbI₃	-3583	0.53	0.28	0.273	1.57

Co-addition of GA and EA → Decrease of E_{total}

$$J = \frac{ne^2 \tau E}{m^*}$$

Possible increase of J_{SC}

◆ Band structures and Molecular dynamics behaviors of MA defect

GA introduction by Born-Oppenheimer molecular dynamics calculations

◆ Changes of microstructures

As-prepared / After 12 months XRD patterns (GA 12.5%+EA 12.5%, GA 10%+EA 10%, GA 5%+EA 5%)

Devices	Time (months)	Lattice constant (Å)	Time (months)	Lattice constant (Å)
GA 5%+EA 5%	0	6.268(0)	12	6.268(0)
GA 10%+EA 10%	0	6.264(0)	12	6.275(0)
GA 12.5%+EA 12.5%	0	6.270(0)	12	6.279(0)

After 12 months → Increase of lattice constants by GA and EA co-addition

Devices	J_{SC} (mA cm^{-2})		V_{OC} (V)		FF		η (%)	
Standard	19.2	19.5	0.820	0.832	0.760	0.663	11.9	10.7
GA 10%	21.3	18.0	0.835	0.861	0.773	0.704	13.9	10.9
GA 20%	21.2	20.6	0.793	0.827	0.634	0.614	10.7	10.4
GA 5%+EA 5%	19.2	19.4	0.803	0.874	0.550	0.673	8.46	13.1
GA 10%+EA 10%	13.4	20.9	0.798	0.905	0.533	0.641	5.71	12.1
GA 12.5%+EA 12.5%	12.0	16.4	0.836	0.950	0.521	0.638	5.23	9.92

Standard — XRD peaks (100, 200, PbI₂, PbICl) As-prepared vs 15 month

GA 12.5%+EA 12.5% — XRD peaks (100, 200, PbI₂, PbICl) As-prepared vs 12 month
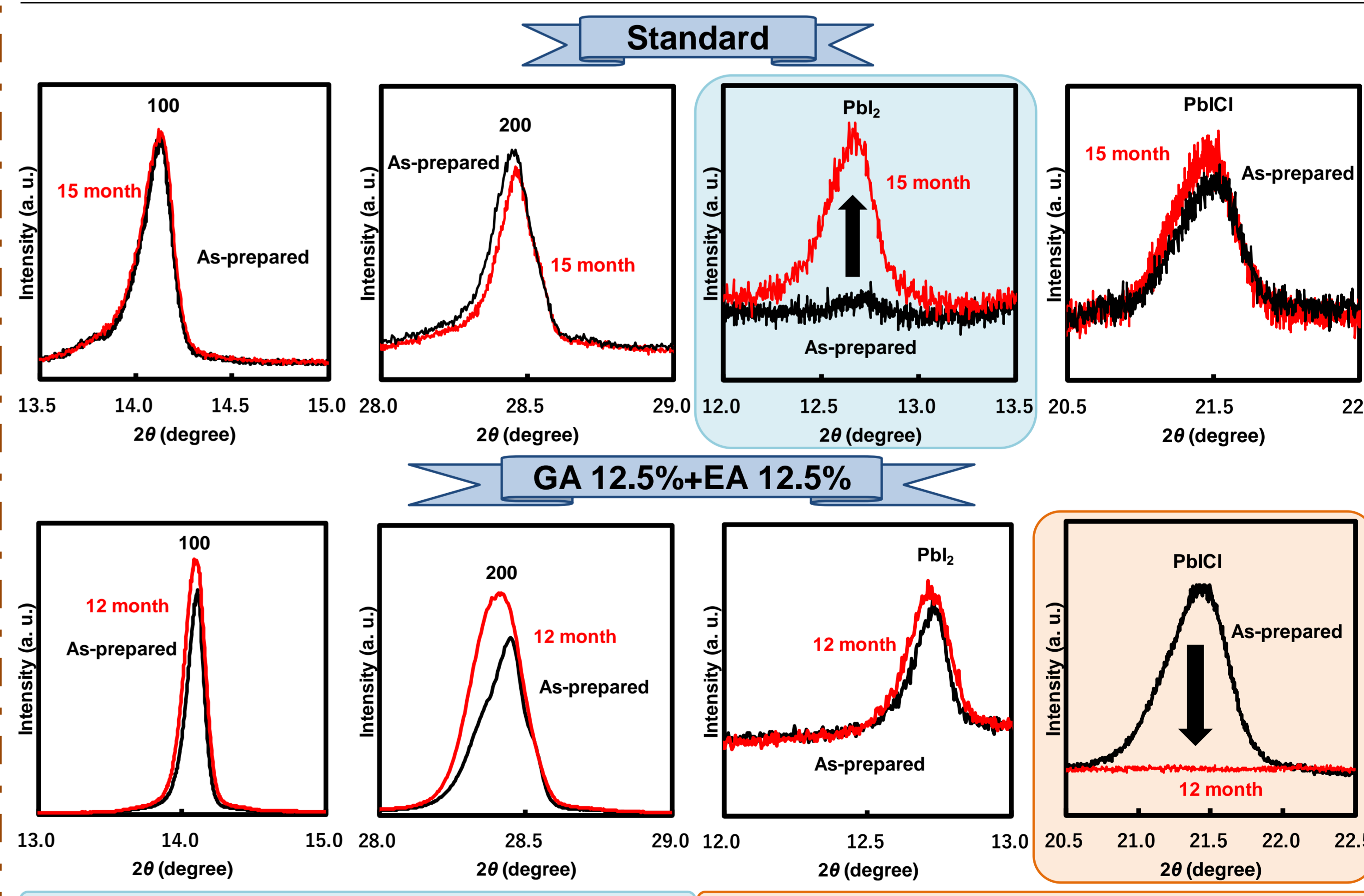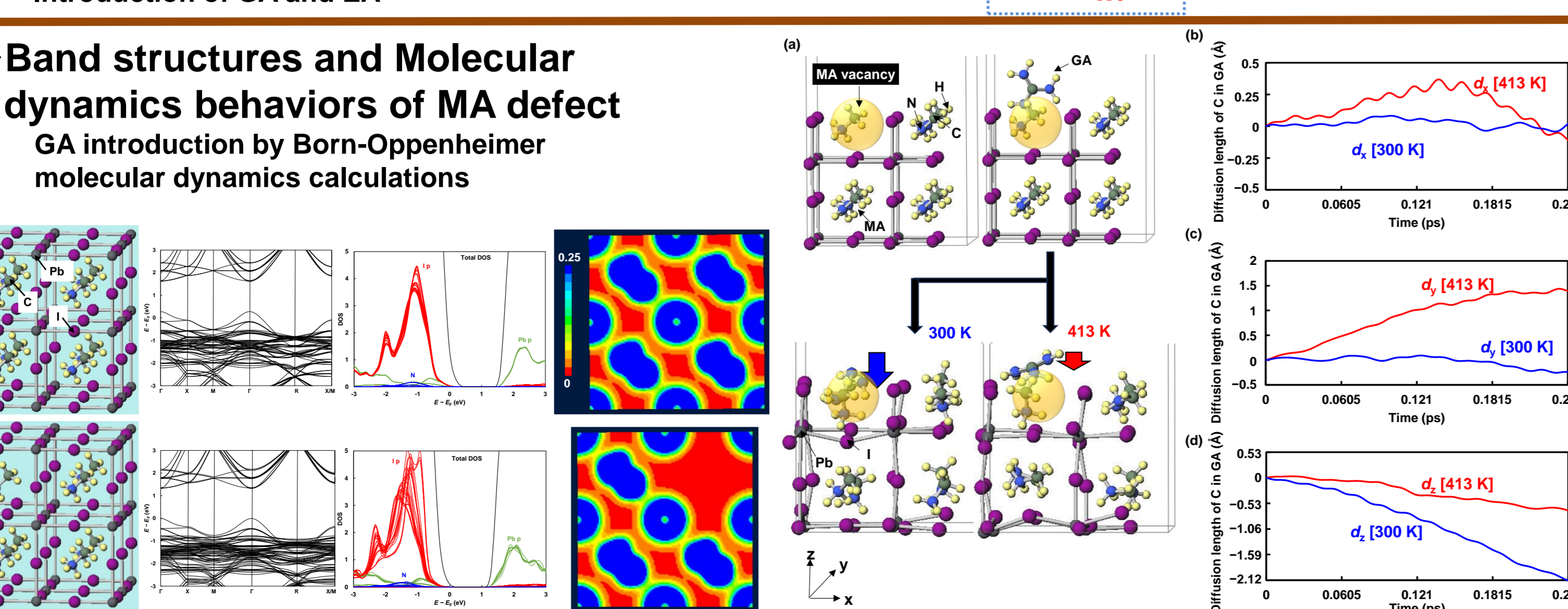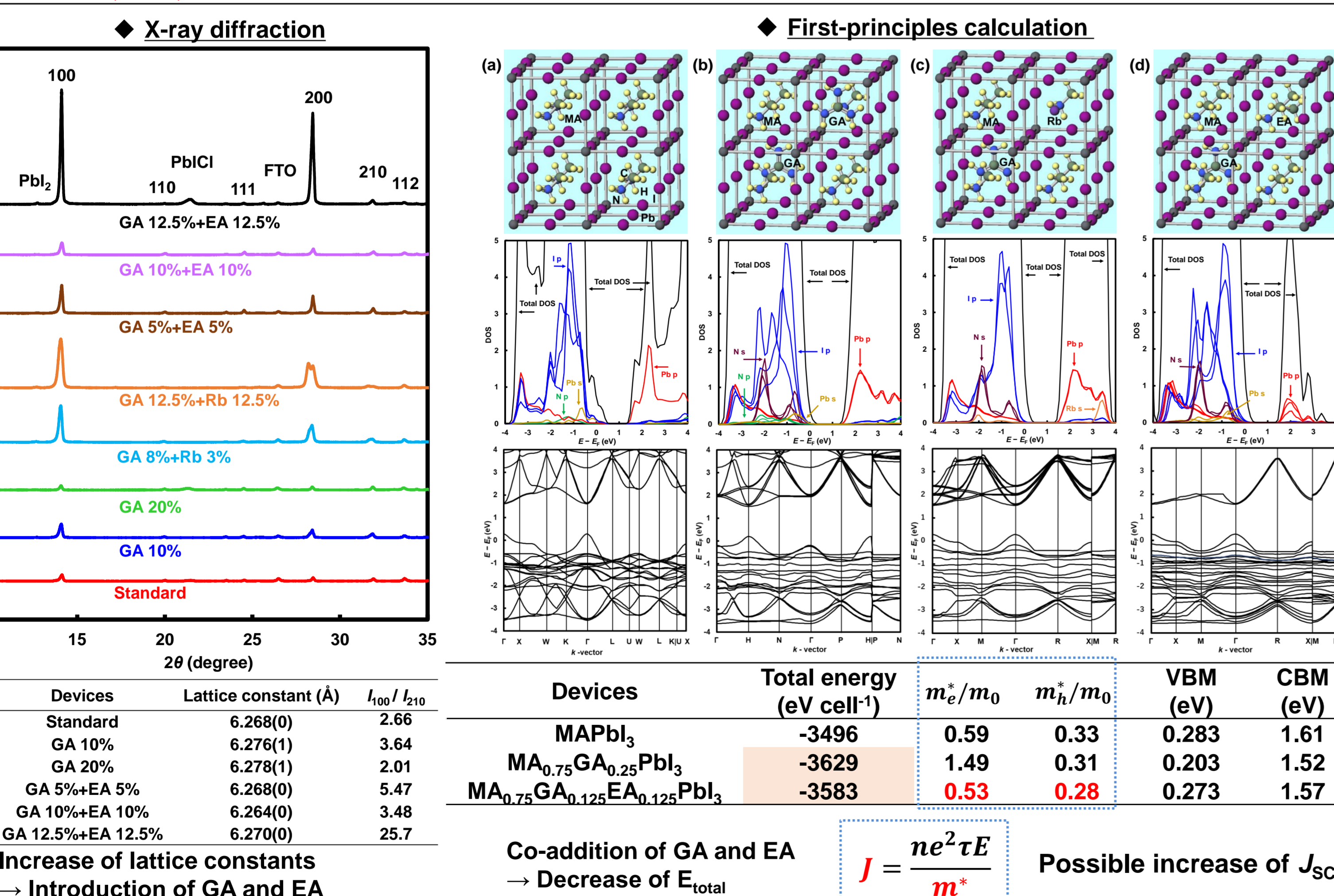
Increase of PbI₂ peak → Degradation of photovoltaic properties by MA desorption

Disappearance of PbICl peak → Increase of perovskite peaks

Conclusion

Effects of the addition of Rb and EA to guanidinium GA-based CH₃NH₃PbI₃ perovskite solar cells were investigated. Lattice constants and the (100)-orientation of EA- and Rb-modified perovskite crystals increased compared with those of as-prepared perovskite. Abnormal increases of lattice constants of the GA- and EA-modified perovskite crystals prepared at 190 °C for 10 min in ambient air were also observed during the room temperature aging, which was due to crystal growth of the perovskites, and these features contributed to increased conversion efficiencies of devices based on the modified perovskites. Addition of GA and EA also effectively improved the photovoltaic properties of the device under indoor light conditions using white light-emitting diodes. First-principles calculations of the density of states and band structures indicated a reduction of the total energy through the addition of Rb or EA, suggesting that the current density was improved by the reduced band gap. vacancies at 300 K, and the experimental and calculated results indicated that the MA vacancies were suppressed by adding GST without annealing.