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Additive effects of lanthanide compound into $CH_3NH_3PbI_3$ perovskite layer on the photovoltaic properties and electronic structure

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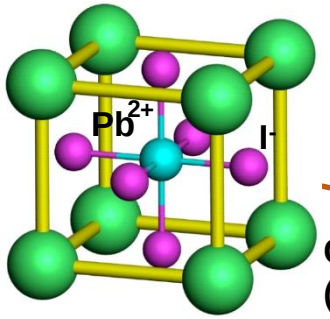
OSAKA GAS CHEMICALS

Introduction

Perovskite solar cell

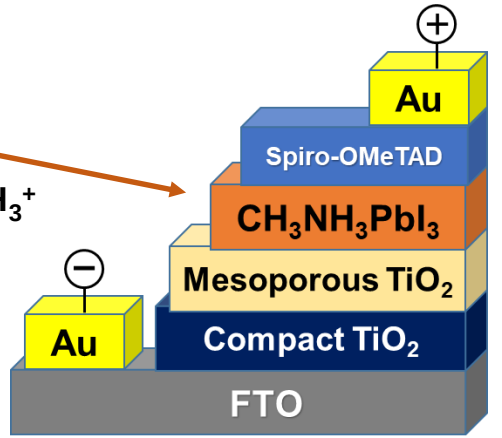
- Elements, Crystal structure
- V_{oc} > 1.0 V Si, E_g ≈ 1.6 eV,
- η ≈ Si, GaAs]
- Conversion region (300 - 800 nm)
- Simple process by spin coating
- Easy to decompose,
- Challenges for stability

Effective mass and carrier mobilities			
	Perovskite	Si	GaAs
m_e^* / m_0	0.2	1.1	0.07
m_h^* / m_0	0.2	0.6	0.5
μ_e (cm^2 / Vs)	5-10	1400	8500
μ_h (cm^2 / Vs)	1-5	450	400
Band gap (eV)	1.57	1.12	1.42

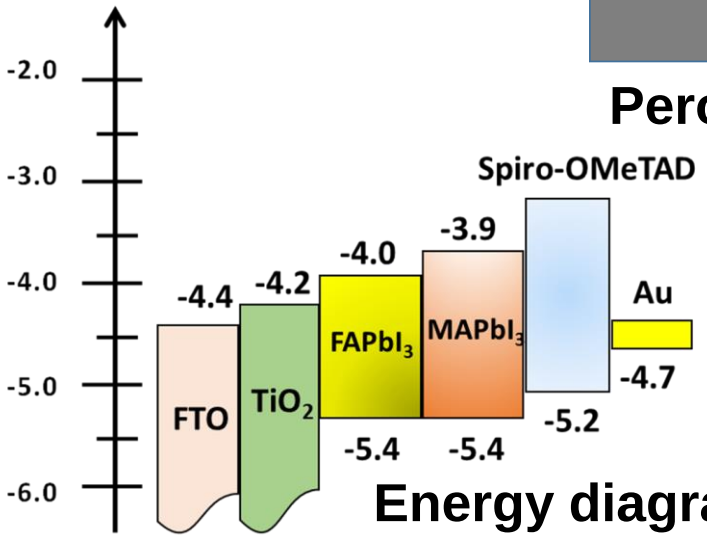


$CH_3NH_3^+$ (MA^+)

Perovskite crystal



Perovskite solar cell



Energy diagram of solar cell

Lanthanoid compounds: Eu (II), Sm (III), Tb (III)

⇒ Stability of the photovoltaic performance

Wang et al., Science 363 (2019) 265–270.

A. Suzuki, T. Oku, Jpn. J. Appl. Phys. 57 (2018) 02CE04-1-7.
A. Suzuki, M. Oe, T. Oku, J. Electron. Mater. 50 (2021) 1980.
A. Suzuki, T. Oku, Heliyon 4 (2018) e00755-1-22, A. Suzuki, T. Oku, Mater. Adv. 2 (2021) 2609-2616.

lanthanide (Ln) compound

4f-spin in Ln is less susceptible to the effect of crystal field

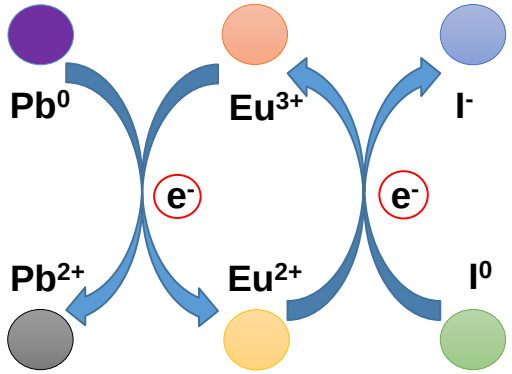
Eu^{3+}: 4f-4f transition Red fluorescence

⇒Up/down conversion materials for solar cell

Eu^{2+}: $4f^6 5d^1$ transition wide fluorescence

Magnetism, high spin state ($4f^7$ $J = S = 7/2$) ($I = 5/2$)

Wang et al., Science 363, 265–270 (2019)

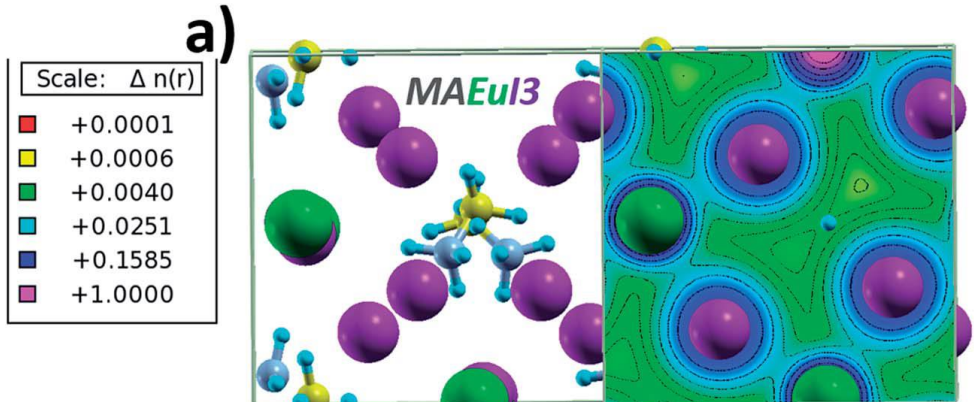


$Eu^{2+} + I^0 \rightarrow Eu^{3+} + I^-$

Eu^{3+} - Eu^{2+} Redox reaction

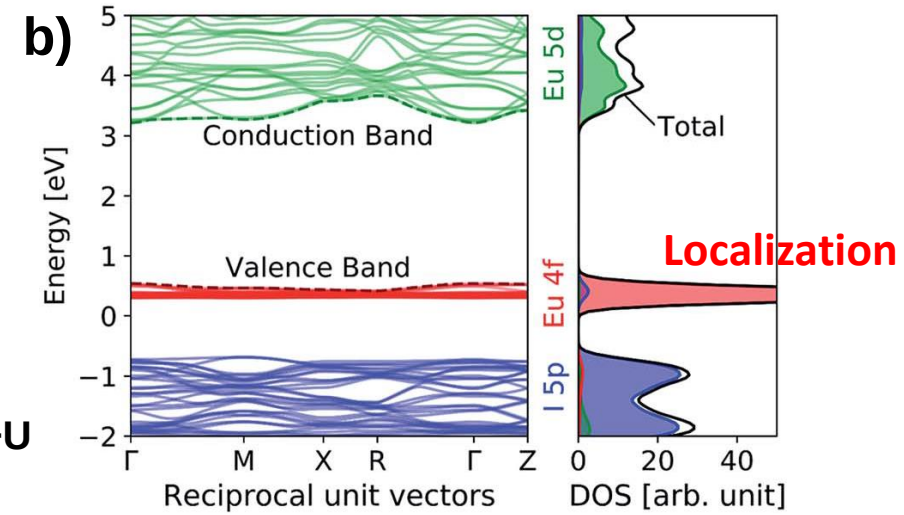
Incorporation of Eu suppressed the decomposition

⇒ Long-term of stability, Improved performance



Charge density of $MAEuI_3$ perovskite calculated by DFT+U

M. Pazoki, et. al. J. Mater. Chem. A, **5** (2017) 23131



Purpose: Electronic structures of lanthanide (Eu, Sm, Tb, Ce) incorporated perovskite crystal were calculated by first-principles calculation, and characterization of lanthanide compound incorporated $CH(NH_2)_2PbI_3$ ($FAPbI_3$) perovskite solar cell was performed for improving the photovoltaic performance.

First-principle calculation

Electron density distribution

Band structure

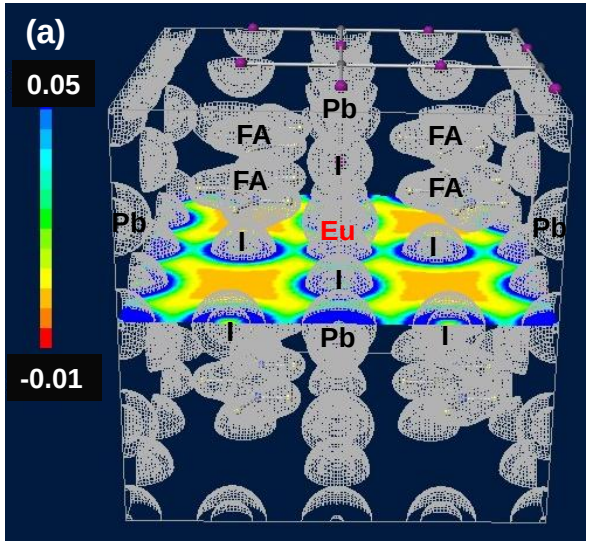
pDOS

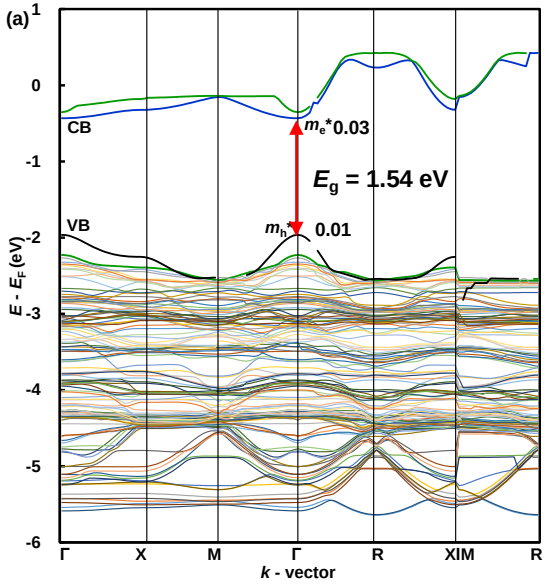
(a) $FAPbEu(II)I_3$

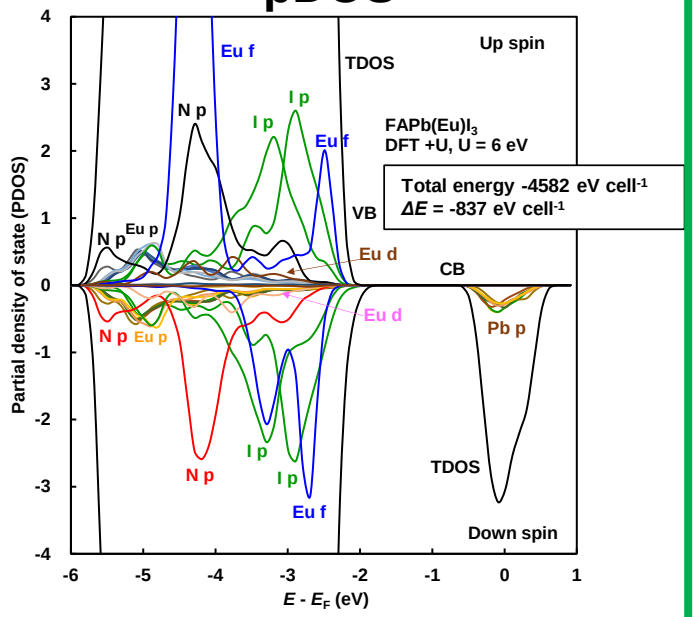
DFT+U, U = 6 eV
k = 8 x 8 x 8
Cubic
a = 12.72 Å

Eu - I band
p, d, f orbital

Eu $4f^7$ $5d$ $6s^2$





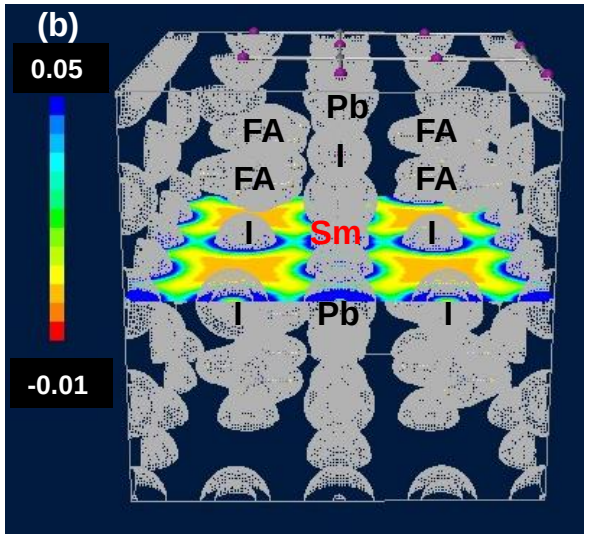


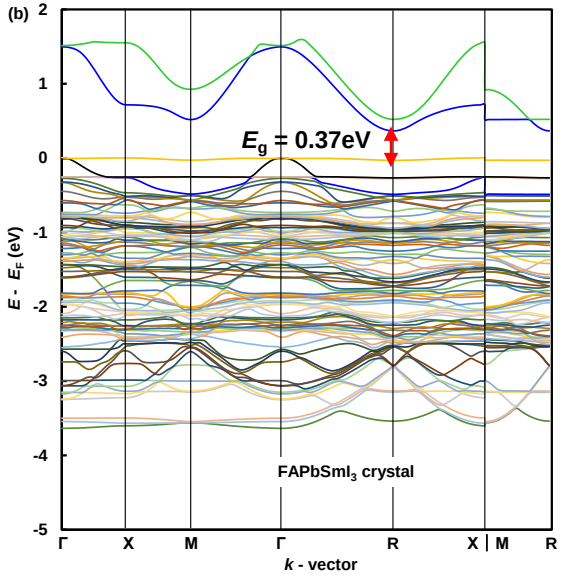
(b) $FAPbSm(II)I_3$

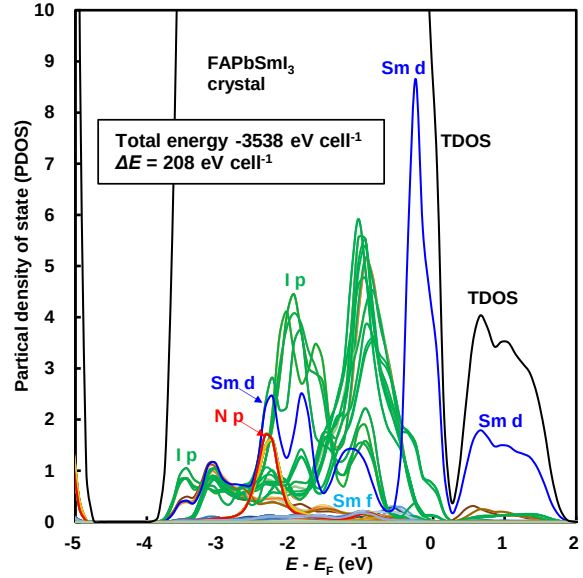
PBE
k = 4 x 4 x 4
Cubic
a = 12.72 Å

Sm - I band
p, d, f orbital

Sm $4f^6$ $5d$ $6s^2$



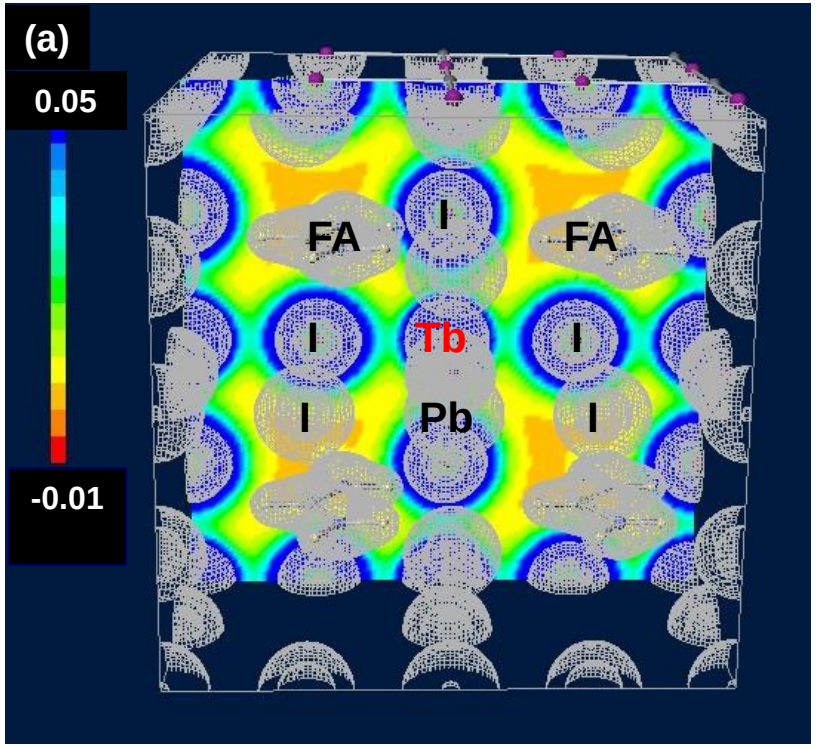




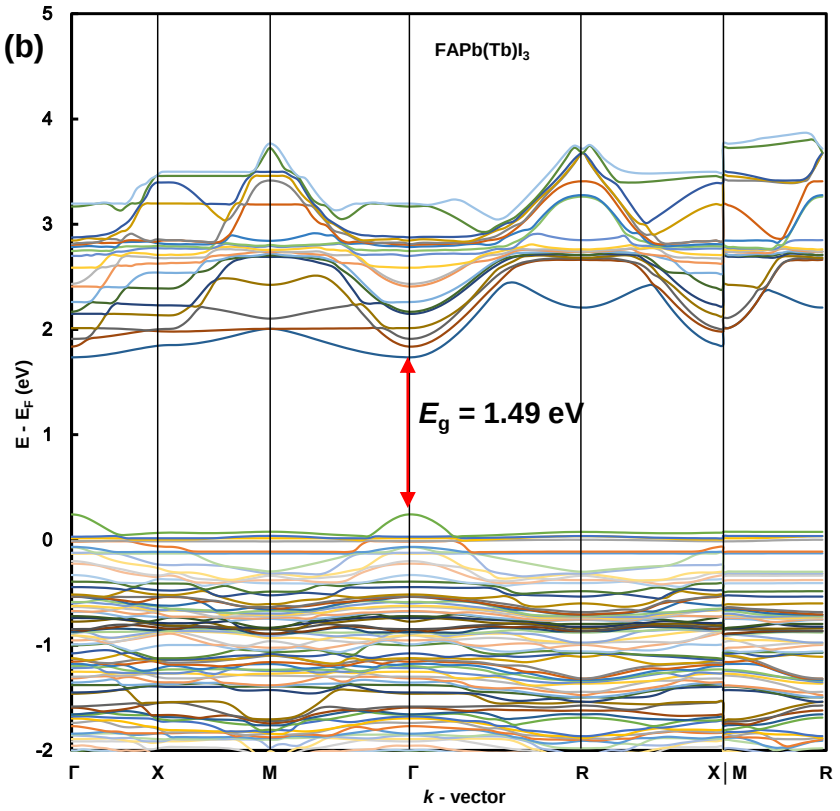
Electron density distribution, band structure, pDOS of (a) $FAPbEu(II)I_3$ and (b) $FAPbSm(II)I_3$ crystal

Electronic structure of FAPbTb(III)I_3

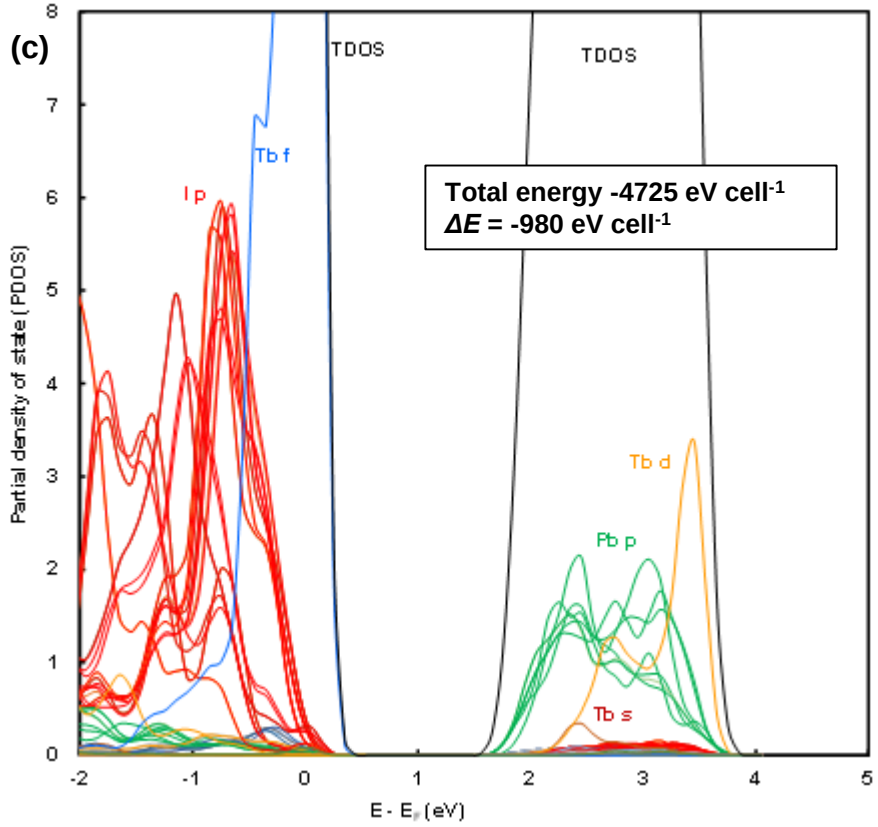
Electron density distribution



Band structure



Partial density of state (PDOS)



(a) Electronic density distribution, (b) band structure and (c) partial density of state (PDOS) of Tb(III)-doped $FAPbI_3$ perovskite crystals

PBE, *k* = 4 x 4 x 4, Cubic, a = 12.72 Å

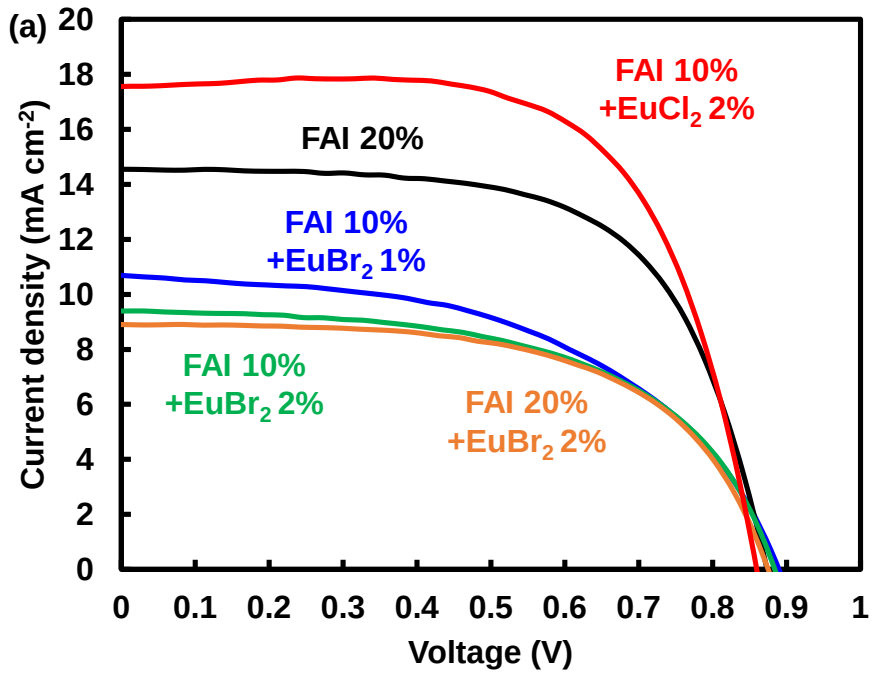
Tb: $4f^9\ 5d\ 6s^2$

Total energies of the doped-$FAPbI_3$ cluster and crystals.

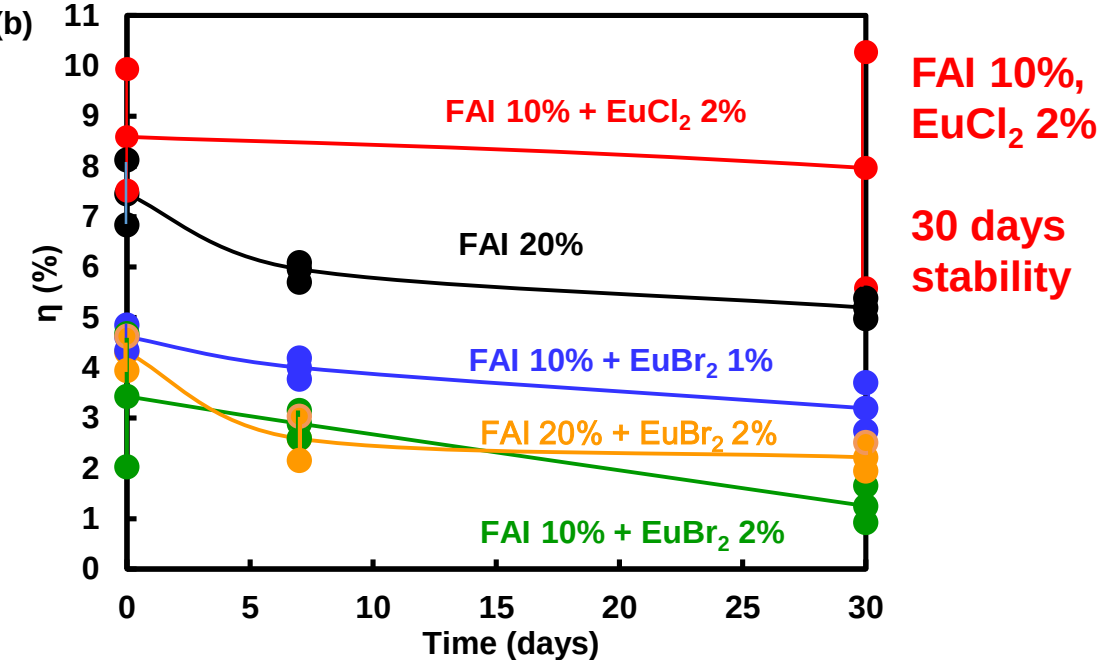
Doped-cluster	Total energy (eV $cell^{-1}$)	ΔE [a] (eV $cell^{-1}$)	
$FAPbI_3$	-6513	0	
Eu^{2+}	-8918	-2405	
Eu^{3+}	-8915	-2402	
Sm^{2+}	-5417	1096	
Tb^{3+}	-5894	619	
Eu^{2+}, Cl^-	-11971	-5458	Stability
Eu^{2+}, Br^-	-8931	-2418	
Doped-crystal	**Total energy (eV $cell^{-1}$)**	**ΔE [a] (eV $cell^{-1}$)**	
$FAPbI_3$	-3745	0	
Eu^{2+}	-4582	-837	Stability
Eu^{3+}	-3714	31	
Sm^{2+}	-3538	207	
Tb^{3+}	-4725	-980	Stability
Ce^{4+}	-3500	245	

[a] ΔE: difference between the total energy of the doped-$FAPbI_3$ and $FAPbI_3$ clusters and crystals

Results and Discussion



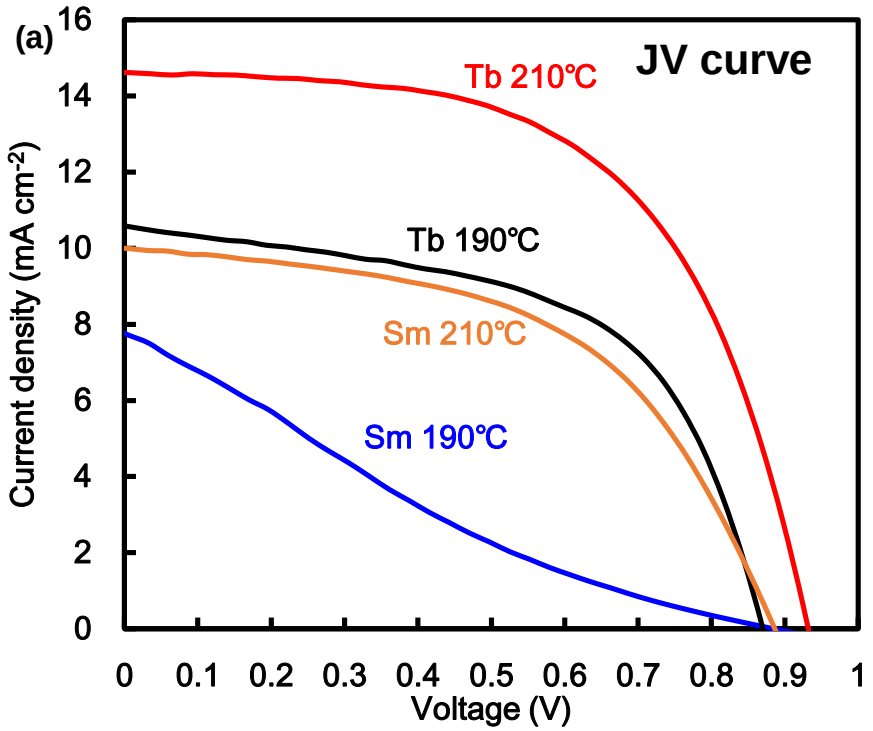
J-V characteristics of the solar cells



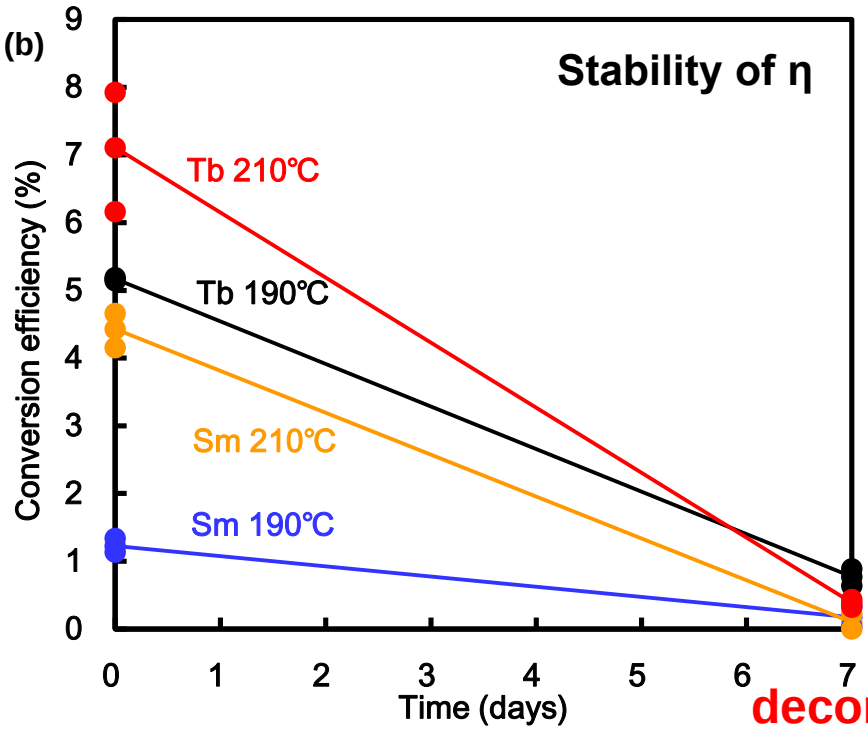
Stabilities of conversion efficiency

Photovoltaic parameters of the perovskite solar cells with FAI and Eu.

Perovskite 190 ℃	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	R_s (Ω cm^2)	R_{sh} (Ω cm^2)	η (%)	η_{ave} (%)
FAI 20%	14.5	0.874	0.640	7.46	3950	8.13	7.40
FAI 10%+$EuCl_2$ 2%	17.6	0.860	0.659	6.57	3960	9.94	8.30
FAI 10%+$EuBr_2$ 1%	10.7	0.889	0.510	14.6	622	4.85	4.66
FAI 10%+$EuBr_2$ 2%	9.40	0.883	0.563	11.5	1690	4.67	3.59
FAI 20%+$EuBr_2$ 2%	8.90	0.875	0.594	12.3	4760	4.62	4.34



J-V characteristics of the solar cells.



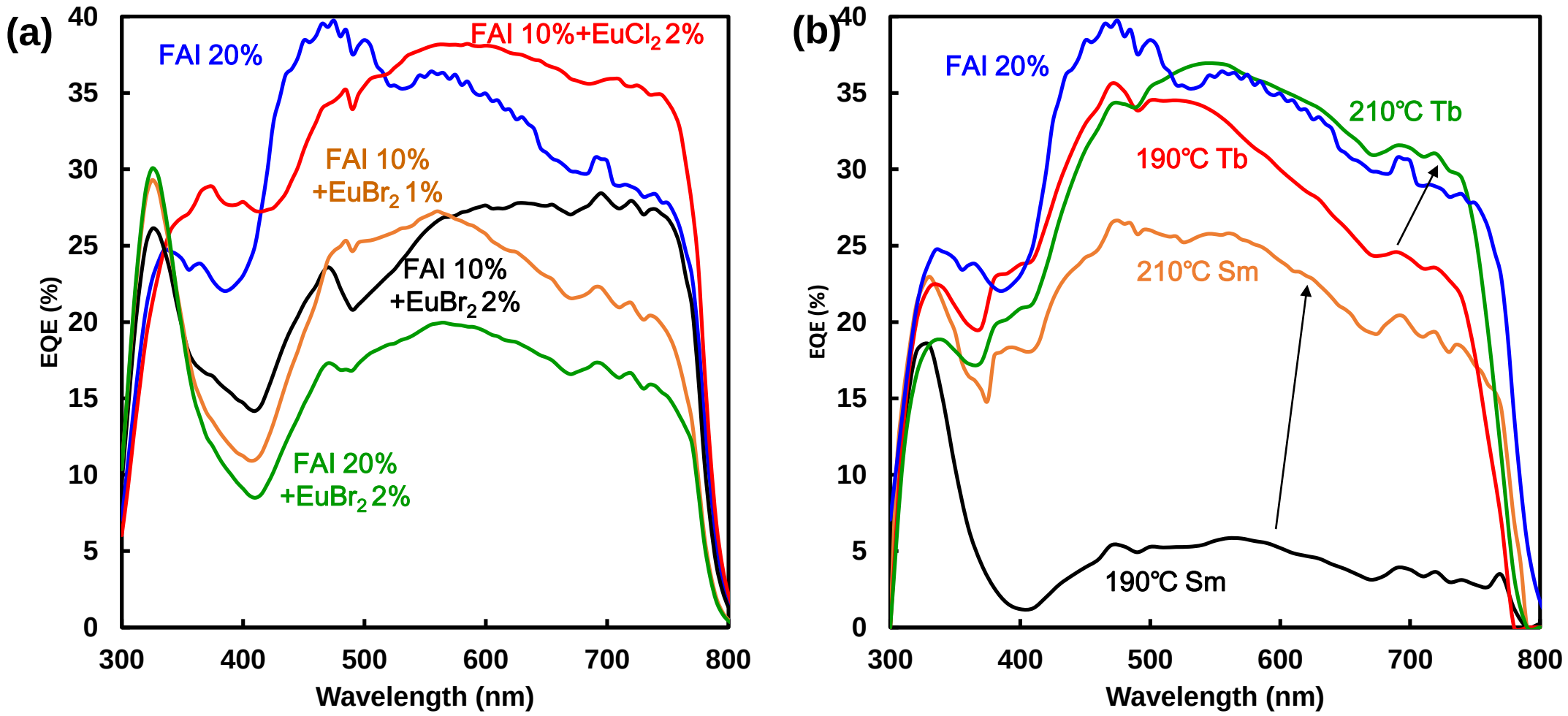
decomposition

Stabilities of conversion efficiency

Photovoltaic properties of perovskite solar cells

Sm, Tb 2%	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	R_s (Ω cm^2)	R_{sh} (Ω cm^2)	η (%)	η_{ave} (%)
190℃ Sm	7.76	0.885	0.195	100	118	1.34	1.20
210℃ Sm	11.2	0.891	0.440	23.6	455	4.79	4.54
190℃ Tb	10.6	0.870	0.564	11.8	421	5.19	5.17
210℃ Tb	14.6	0.932	0.582	10.9	2030	7.93	7.23

External quantum efficiency (EQE)



EQE of the perovskite solar cells with (a) Eu, FA and (b) Sm or Tb.

FAI 10%, $EuCl_2$ 2% EQE Up, Tb, Sm 190℃→210℃ EQE increased

Conclusion

Electronic structure of lanthanide incorporate perovskite crystal was expected by first-principles calculation. The experimental investigation was performed.

Incorporation of Eu promoted the charge transfer, increasing J_{sc} related to η. Localization of d, f orbital of Sm, Tb, Ce near VB and CB suppressed the carrier diffusion, decreasing J_{sc} related to η.

The calculation prediction could be proved from the experiments.