Electronic structures and photovoltaic properties of copper−, sodium− and ethylammonium−added $CH_3NH_3PbI_3$ perovskite compound

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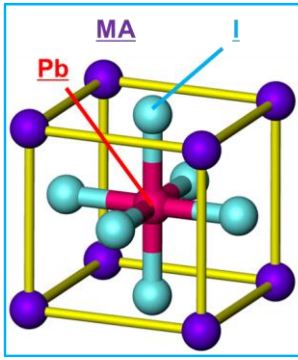
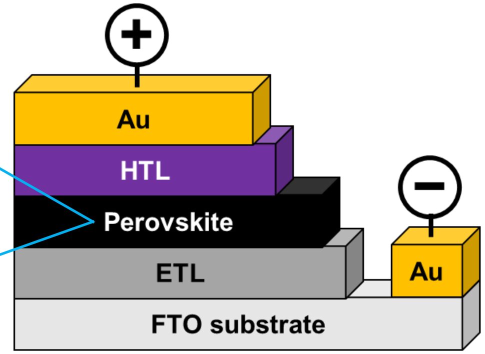
Introduction



Perovskite crystal structure



Device structure

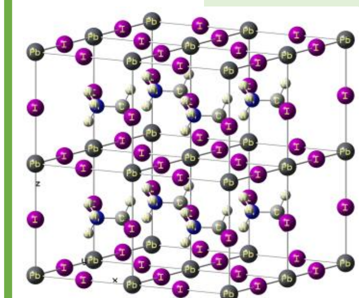
MA : Methyl ammonium
HTL : Hole transport layer
ETL : Electron transport layer

Experiment

Device fabrication

- ◯ Current-voltage characteristics
- ◯ External quantum efficiency (EQE)
- ◯ X-ray diffraction (XRD)
- ◯ Device durability

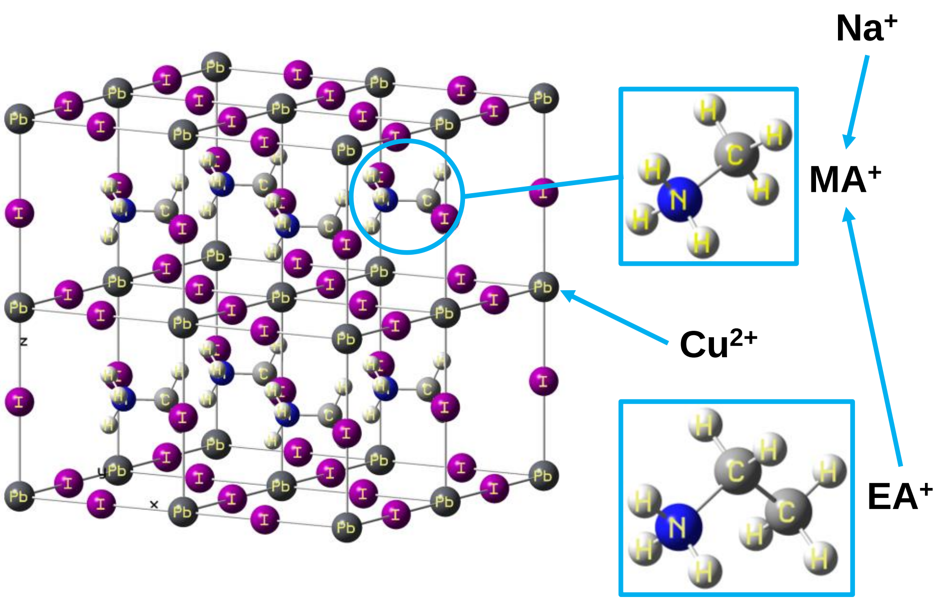
Calculation



Crystal structure modeling

- ◯ Total energy
- ◯ Band structure
- ◯ Partial density of state
- ◯ Electron density distribution

Introduction



MA : Methyl ammonium
EA : Ethyl ammonium

○ <u>Effects of adding copper</u>

→ Increase in particle size
Homogenization of surface morphology

K. L. Wang, *et al*. Nano Lett. 19, 5176-5184 (2019)
M. Jahandar, *et al*. Nano Energy 27, 330-339 (2016)

○ <u>Effects of adding alkali metals</u>

→ Decrease in hysteresis, etc.
Inherent additive effects

S. G. Kim, *et al*. J. Mater. Chem. A 7, 18807 (2019)
C. Baena, *et al*. Science 363, 627-631 (2019)

○ <u>First-principles calculations</u>

Copper and alkali metals substitution destabilizes crystal structure

→ Stable organic cations were introduced for stability

D. Liu, *et al*. RSC Adv. 9, 7356 (2019)
M. Mateen, *et al*. Sci. China Mater. 63, 2477-2486 (2020)

○ <u>Purpose of this study</u>

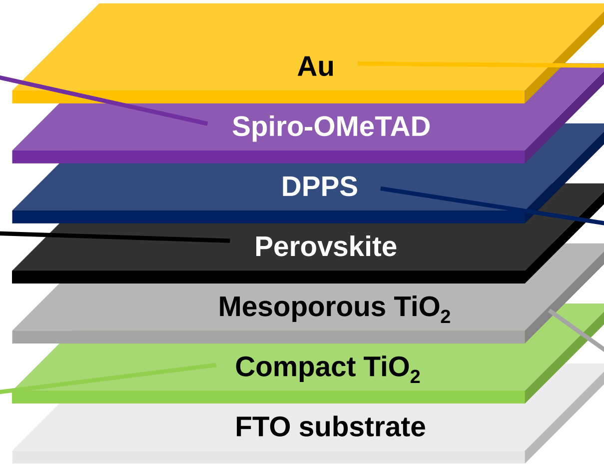
Investigation of the effects of adding copper, alkali metals, and organic cations to perovskite crystals through experiments and first-principles calculations

Device fabrication

Spin-coating spiro-OMeTAD solution

Spin-coating perovskite precursor solution

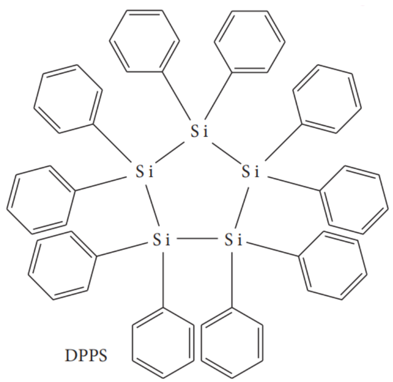
1. **Spin-coating compact TiO_2 precursor solution**
2. **Annealing at 550 °C for 30 min**



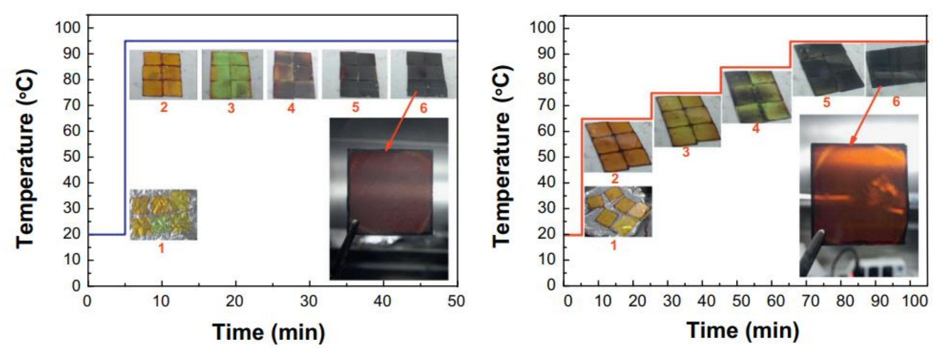
Vacuum deposition of Au

1. **Spin-coating perovskite precursor solution and DPPS**
2. **Annealing at 90-160 °C**

1. **Spin-coating mesoporous TiO_2 precursor solution**
2. **Annealing at 550 °C for 30 min**



T. Oku, *et al*. Coatings 11, 665 (2021)



L. Huang, *et al*. Sol. Energy Mater. Sol. Cells 141, 377-382 (2015)

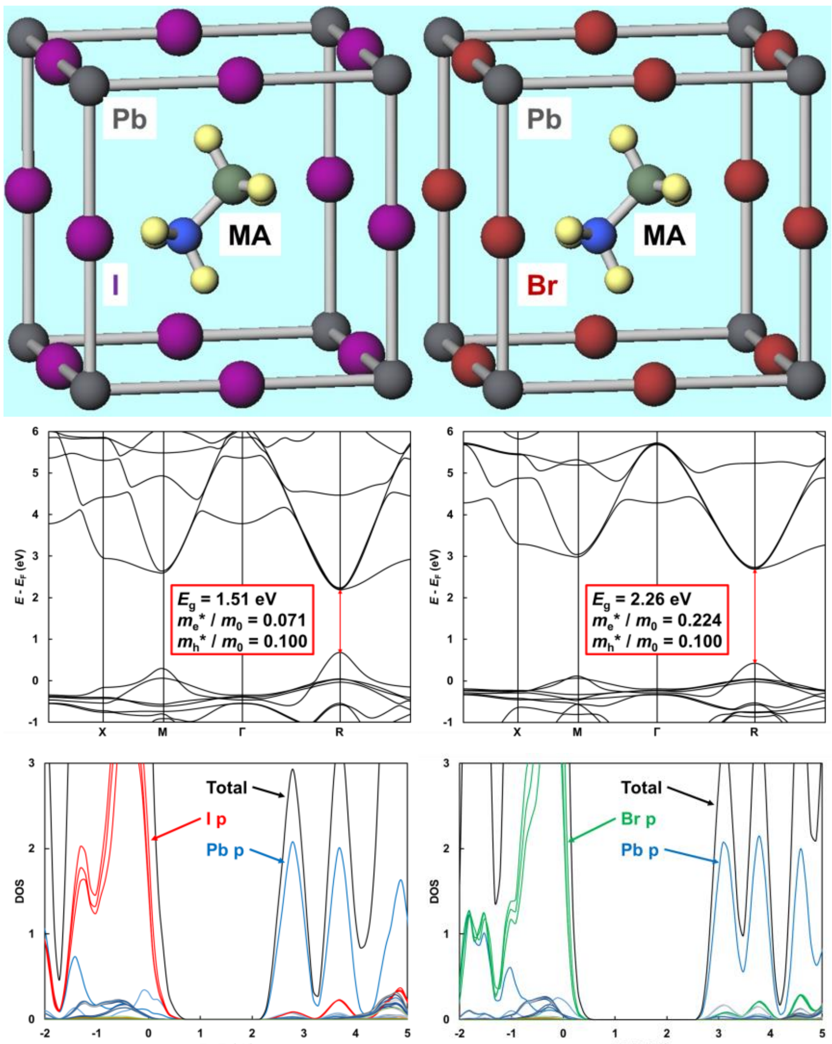
Addition of DPPS to enhance heat resistance of perovskite crystals

Increase of heat treatment temperature in steps to improve quality of the perovskite film

First principles calculations

Effect of Br substitution on energy gap

$MAPbI_3$ **$MAPbBr_3$**



Model	ΔE (eV)	E_g (eV)	m_e^*/m_0	m_h^*/m_0
$MAPbI_3$	0	1.51	0.071	0.100
$MAPbBr_3$	−160	2.26	0.224	0.100

E : Total energy
E_g : Energy gap
m_e^*/m_0, m_h^*/m_0 :
Effective mass ratio of electrons and holes

$$V_{OC} \approx \frac{E_g}{q} - \frac{kT}{q}\log\left(\frac{A}{J_{SC}}\right)$$

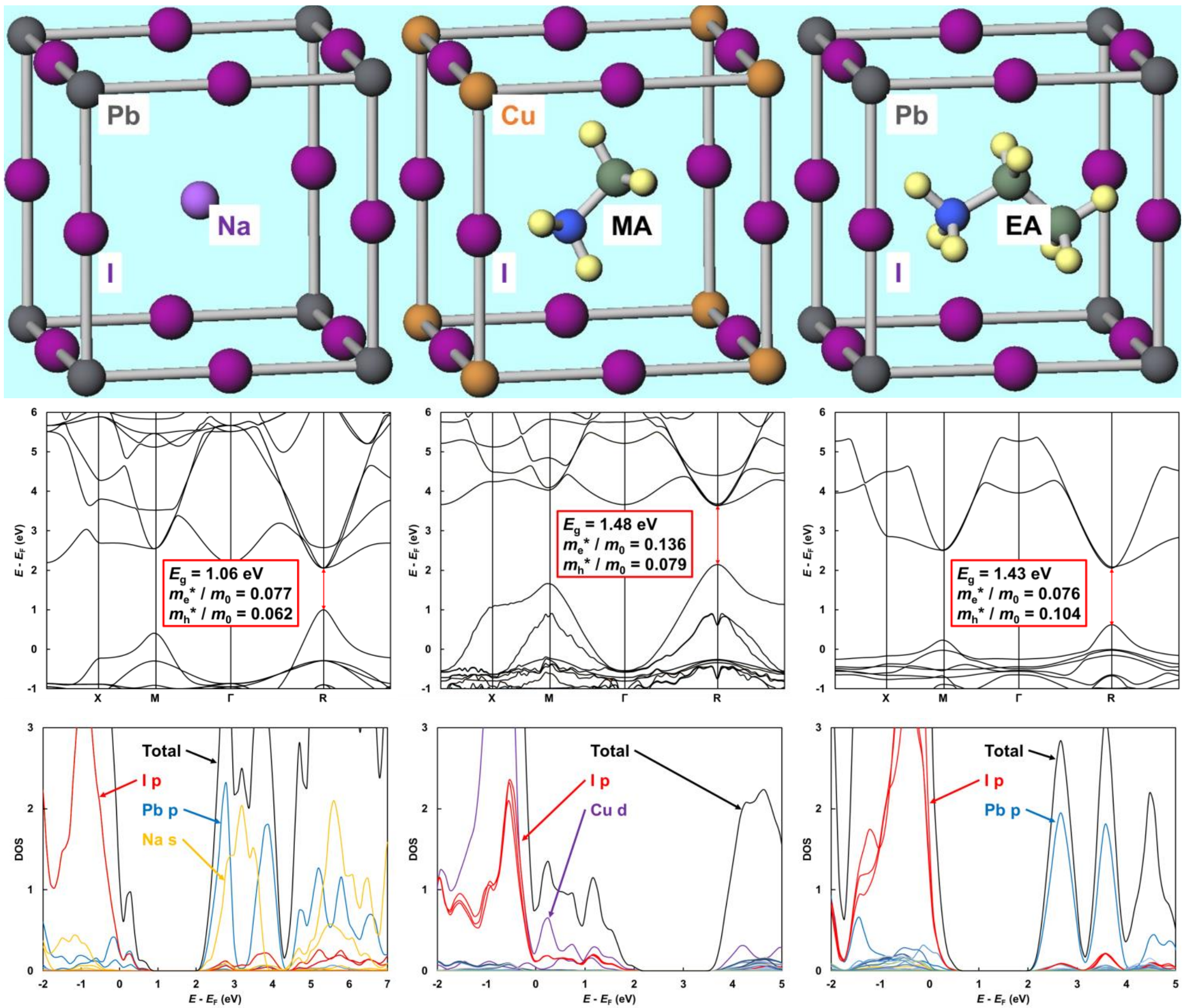
V_{OC} : Open-circuit voltage
E_g : Energy gap

Br substitution increases E_g
→ Possibility to improve V_{OC}

First principles calculations

Effect of Cu, Na and EA on crystal structure stability

$NaPbI_3$ | $MACuI_3$ | $EAPbI_3$



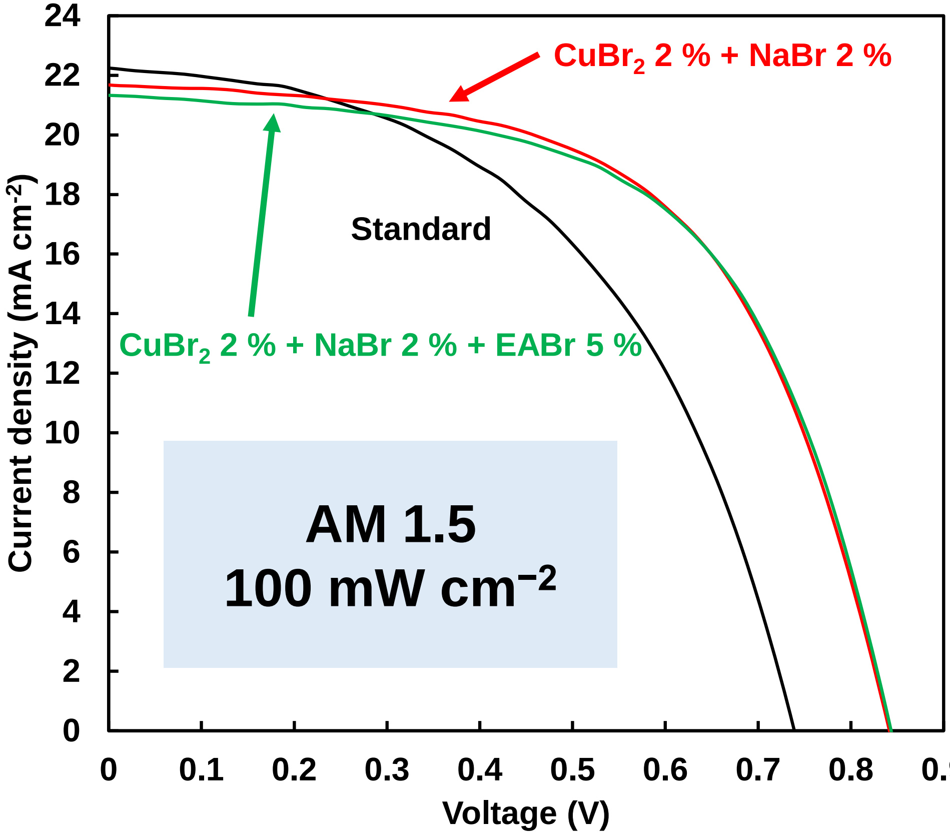
Model	ΔE (eV)
$MAPbI_3$	0
$NaPbI_3$	+510
$MACuI_3$	+980
$EAPbI_3$	−180

○ **Cu, Na substitution**
→ **Destabilization** of crystal structure

○ **EA substitution**
→ **Stabilization** of crystal structure

Results and discussion

J–V curves and parameters



Calculation

$MAPbI_3$ E_g=1.51 eV

$MAPbBr_3$ E_g=2.26 eV

Br substitution increases E_g

$$V_{OC} \approx \frac{E_g}{q} - \frac{kT}{q}\log\left(\frac{A}{J_{SC}}\right)$$

V_{OC} : Open circuit voltage

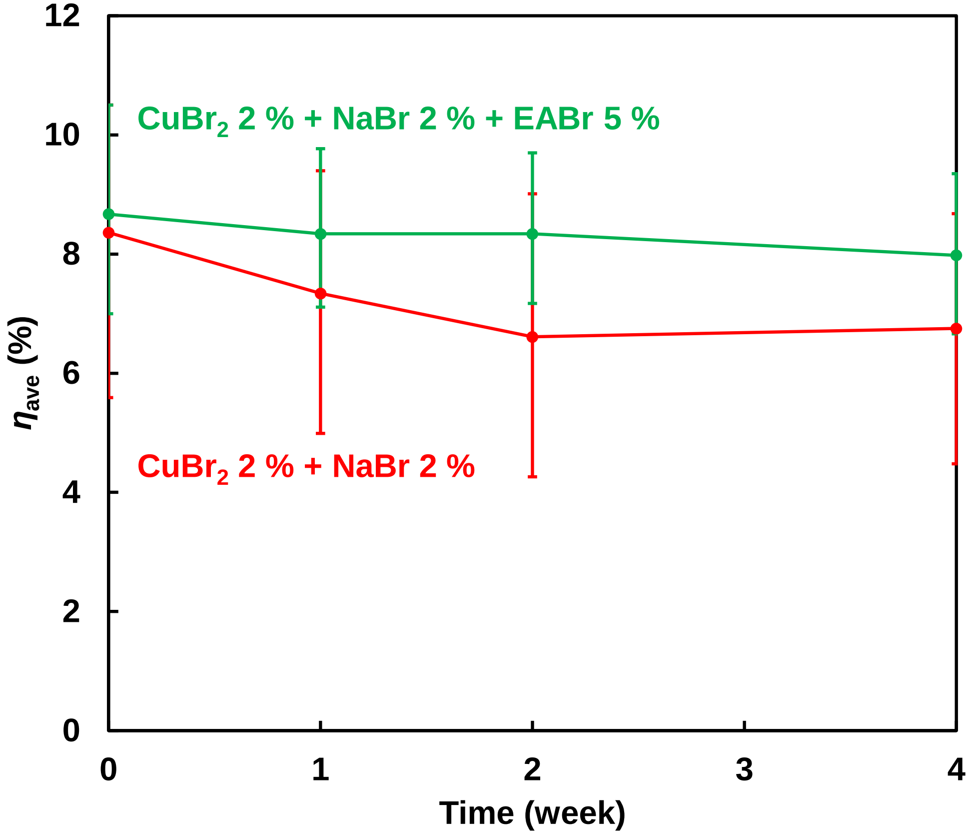
E_g : Energy gap

Increase of E_g contributes to higher V_{OC}

Devices	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)
Standard	22.2	0.739	0.497	4.18	383	8.17	5.82	1.55
$CuBr_2$ 2 % NaBr 2 %	21.7	0.841	0.578	5.93	594	10.5	8.36	1.56
Cu 2 % Na 2 % EABr 5 %	21.3	0.843	0.585	5.12	558	10.5	8.67	1.57

Results and discussion

Total energies and device durability



Calculation

○ Total energy (keV $cell^{-1}$)

$MAPbI_3$: −3.50
$NaPbI_3$: −2.99
$MACuI_3$: −2.52
$EAPbI_3$: −3.68

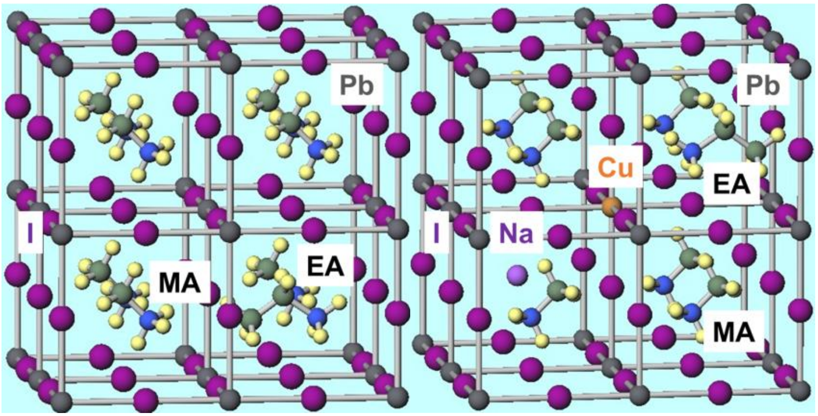
Stabilization of crystal structure by EA substitution
→ Enhanced device durability

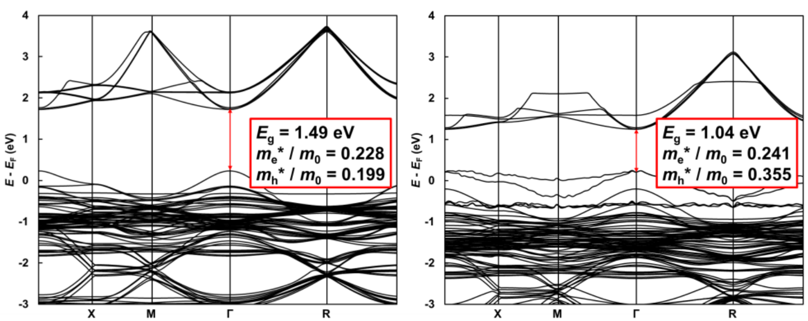
Devices	η_{ave} (%)				Stability (%)
	0 week	1 week	2 weeks	4 weeks	
$CuBr_2$ 2 % NaBr 2 %	8.36	7.34	6.61	6.75	79.1
Cu 2 % Na 2 % EABr 5 %	8.67	8.34	8.34	7.98	96.2

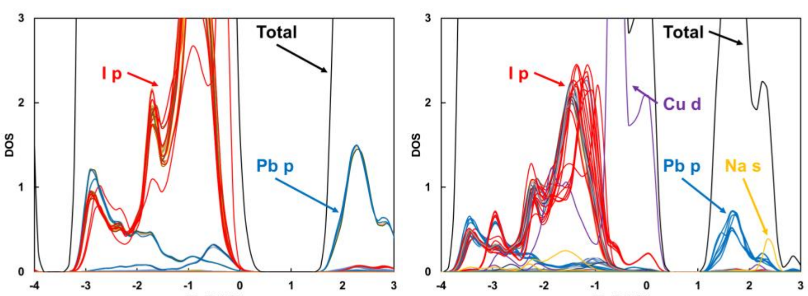
First principles calculations

Results of first-principles calculations using the partial substitution structure model

EA 12.5 % **EA Cu Na 12.5 %**







Model	ΔE (eV)	E_g (eV)	m_e^*/m_0	m_h^*/m_0
EA 12.5 %	0	1.49	0.228	0.199
EA Cu Na 12.5 %	+200	1.04	0.241	0.355

m_h^*/m_0 : Effective mass ratio of holes

○ **Cu and Na substitution**

→ Decrease in E_g

Increase in m_h^*

Experiment

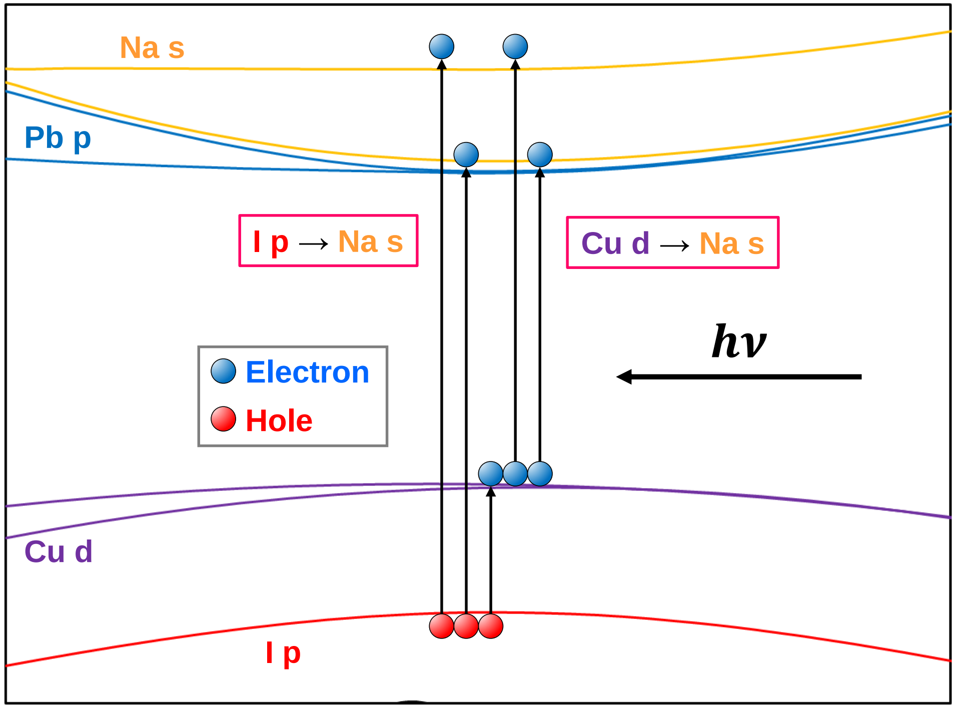
○ **Cu addition**

E_g : 1.55→1.56 eV, η : 8.17→10.5 %

→ Results of experiments and calculations don't correspond

Results and discussion

Model of the excitation process



Calculation

○ Cu substitution

E_g : 1.49→1.00 eV

m_h^*/m_0 : 0.199→0.352

Experiment

○ Cu addition

E_g : 1.55→1.56 eV

η : 8.17→10.5 %

The Cu d orbital level functions as an acceptor level

I − p→Cu − d

▸▸▸ Acceleration of carrier generation

Cu − d, I − p→Na − s

▸▸▸ Decrease in carrier recombination

Conclusion

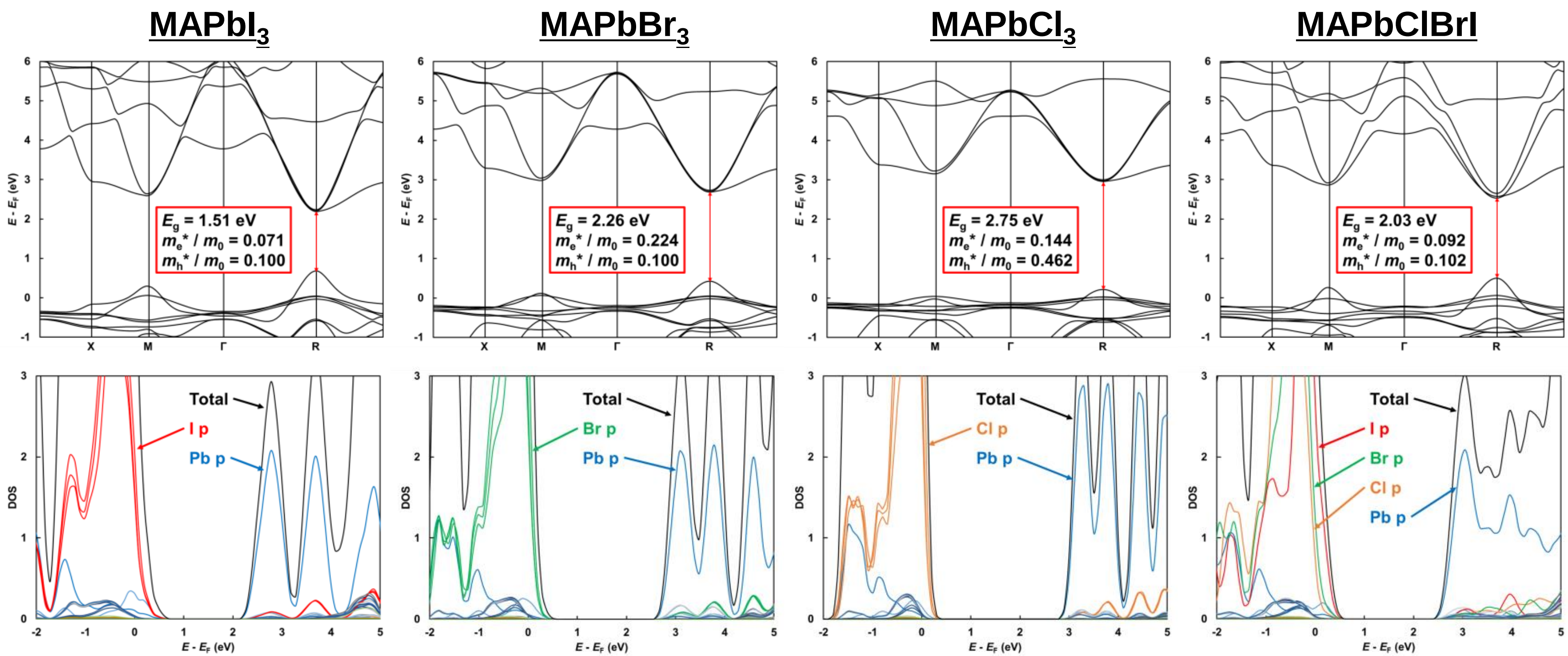
○ **Halogen substitution**
→ Affects energy gap
▸▸▸ **<u>Correspondence between calculation and experimental results</u>**

○ **Stabilization of crystal structure by EA substitution**
→ Enhanced device durability
▸▸▸ **<u>Possibility of predicting durability by first-principles calculations</u>**

○ **Co-adding effects of Cu and Na are discussed using the band structure**
▸▸▸ **<u>Possibility of accelerated carrier generation and reduced loss of generated carriers</u>**

◎ **A method to study the effects of adding compounds using first-principles calculations and experimental results**
▸▸▸ **<u>Applicable for use with other alkali metals and organic cations</u>**

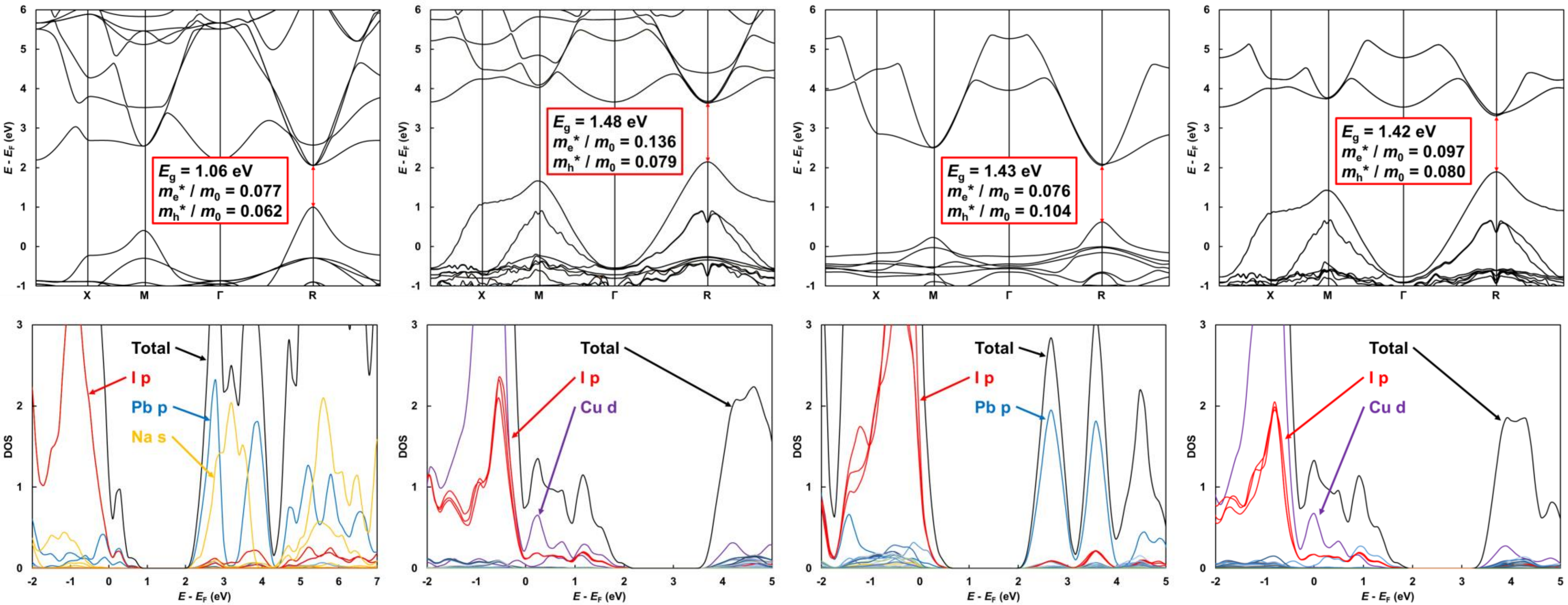
Supporting information



Model	Total energy (keV)	Energy gap (eV)	m_e^*/m_0	m_h^*/m_0
$MAPbI_3$	-3.50	1.51	0.071	0.100
$MAPbBr_3$	-3.66	2.26	0.224	0.100
$MAPbCl_3$	-3.78	2.75	0.144	0.462
MAPbClBrI	-3.64	2.03	0.092	0.102

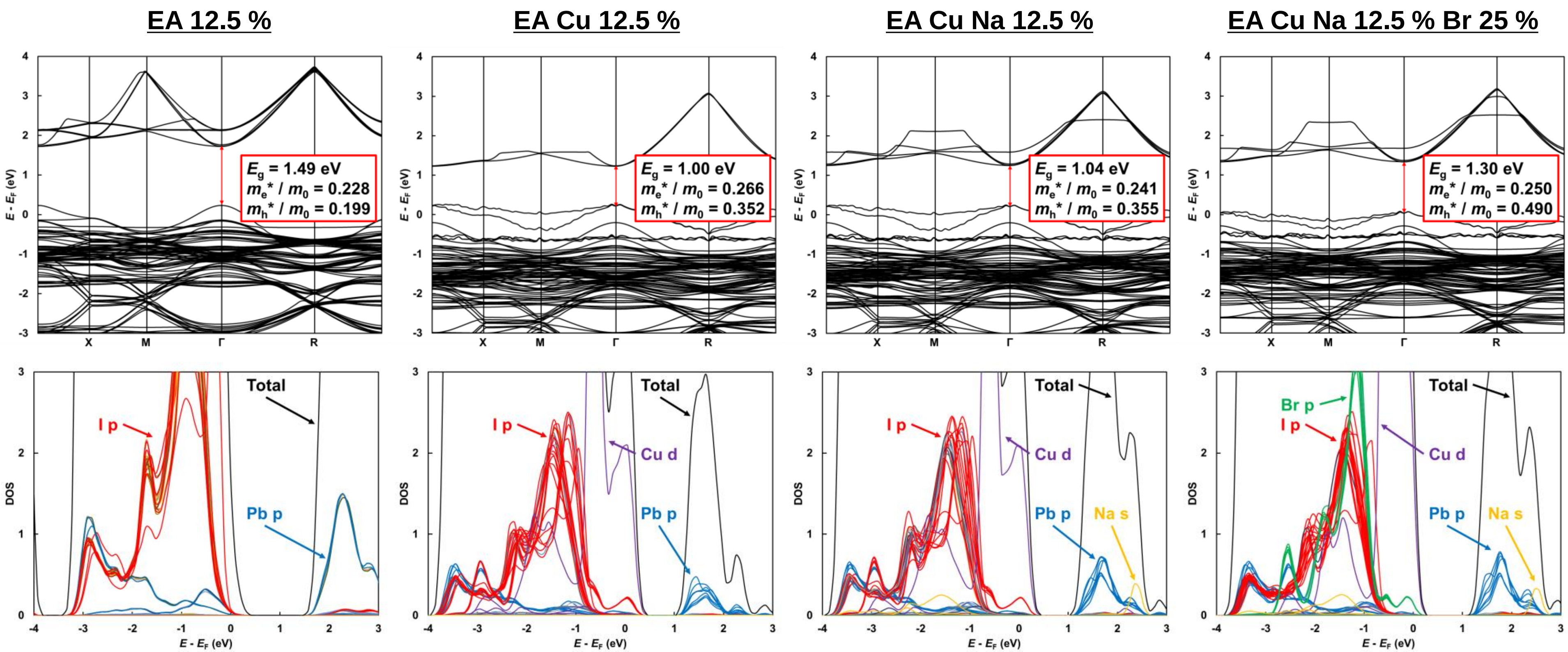
Supporting information

NaPbI$_3$ MACuI$_3$ EAPbI$_3$ EACuI$_3$



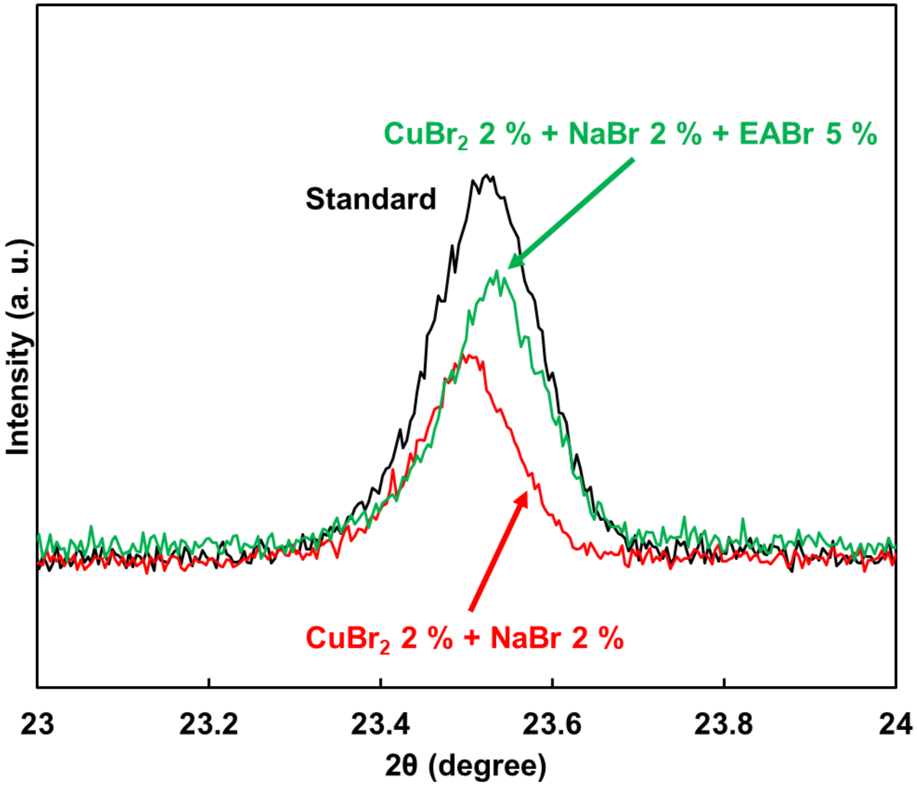
Model	Total energy (keV)	Energy gap (eV)	m_e^*/m_0	m_h^*/m_0
NaPbI$_3$	-2.99	1.06	0.077	0.062
MACuI$_3$	-2.52	1.48	0.136	0.079
EAPbI$_3$	-3.68	1.43	0.076	0.104
EACuI$_3$	-2.71	1.42	0.097	0.080

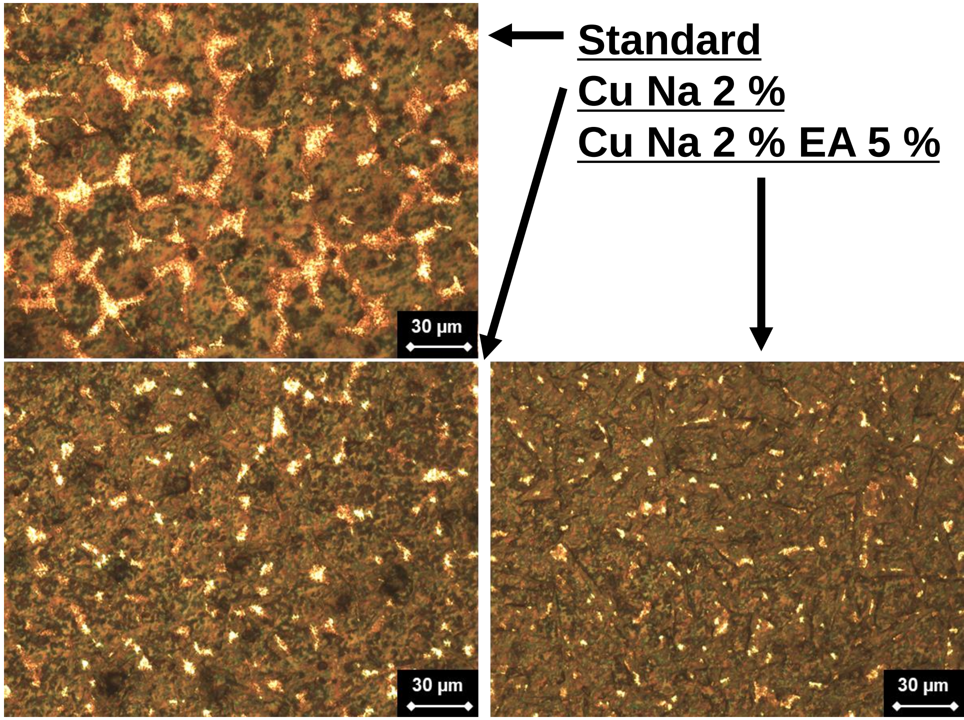
Supporting information



Model	Total energy (keV)	Energy gap (eV)	m_e^*/m_0	m_h^*/m_0
EA 12.5 %	-3.52	1.49	0.228	0.199
EA Cu 12.5 %	-3.39	1.00	0.266	0.352
EA Cu Na 12.5 %	-3.32	1.04	0.241	0.355
EA Cu Na 12.5 % Br 25 %	-3.36	1.30	0.250	0.490

Supporting information





Devices	I_{100}/I_{210}	Lattice constant (Å)	Crystallite size (Å)	I_{211} (tetragonal)
Standard	8.7	6.262(1)	697	1.00
$CuBr_2$ 2 % NaBr 2 %	2.6	6.271(1)	679	0.60
$CuBr_2$ 2 % NaBr 2 % EABr 5 %	3.1	6.261(1)	674	0.81