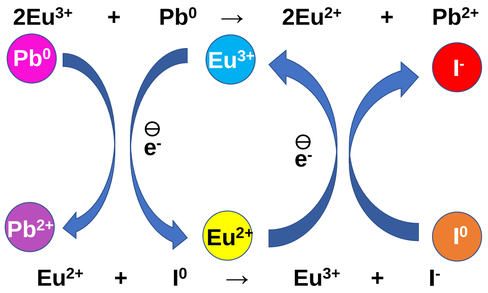
First-principles calculation analysis on electronic structures and molecular dynamics of gadolinium-doped $FAPbI_3$

Atsushi SUZUKI, and Takeo OKU, Department of Materials Chemistry, The University of Shiga Prefecture, Japan

Introduction

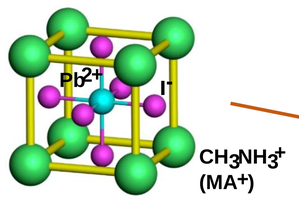
Perovskite solar cell

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

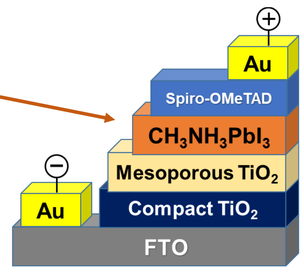


Eu^{3+}-Eu^{2+} Redox reaction

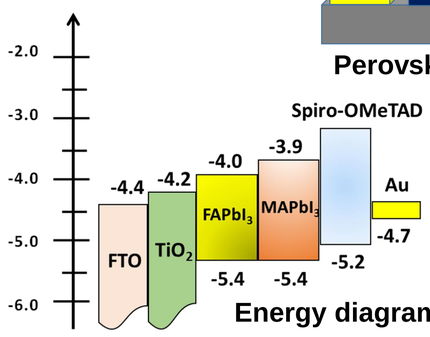
Wang et al., Science 363 (2019) 265–270.



Perovskite crystal



Perovskite solar cell



Energy diagram of solar cell

Lanthanide: Eu (II), Sm (III), Tb (III), Gd (II), Nd (II)

Fluorescence, Wavelength conversion, Redox reaction ⇒ photovoltaic properties Improved

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.
A. Suzuki, T. Oku, J. J. Appl. Phys. 62 (2023) SK1006.

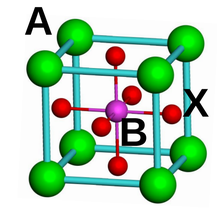
Cs, Pb-free perovskite crystal
η, band gap improved

Estimative index for ABX_3 perovskite crystal structure

MA^+ : $CH_3NH_3^+$
FA^+ : $NH{=}CHNH_2^+$
X^- : I^-, Cl^-, Br^-

tolerance factor (t) $t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$

A site		B site		X site	
MA^+	217 pm	Pb^{2+}	119 pm	Cl^{2-}	181 pm
FA^+	253 pm	Eu^{2+}	117 pm	Br^{2-}	196 pm
		Eu^{3+}	94.7 pm	I^{2-}	220 pm
		Sm^{3+}	95.8 pm		
		Tb^{3+}	92.3 pm		



Perovskite crystal

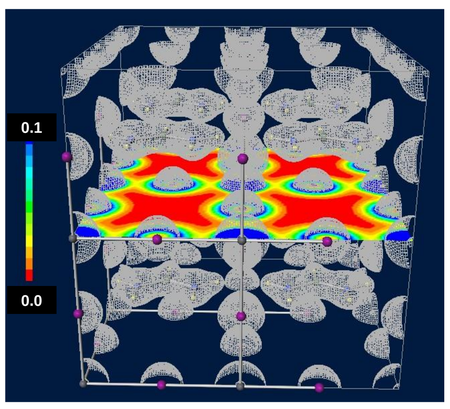
Perovskite layer	Tolerance factor (t)
FAI 20%	0.927
FAI 10% + $EuCl_2$ 2%	0.920
FAI 10% + $EuBr_2$ 1%	0.919
FAI 10% + $EuBr_2$ 2%	0.920
FAI 20% + $EuBr_2$ 2%	0.928
FAI 20% + Sm 2%	0.928
FAI 20% + Tb 2%	0.928

Purpose

Material design of gadolinium doped $FAPbI_3$ perovskite crystals, and first-principles calculation analysis on electronic structure and molecular dynamics were performed for application of the photovoltaic devices with the stability of photovoltaic performance.

Results and Discussion

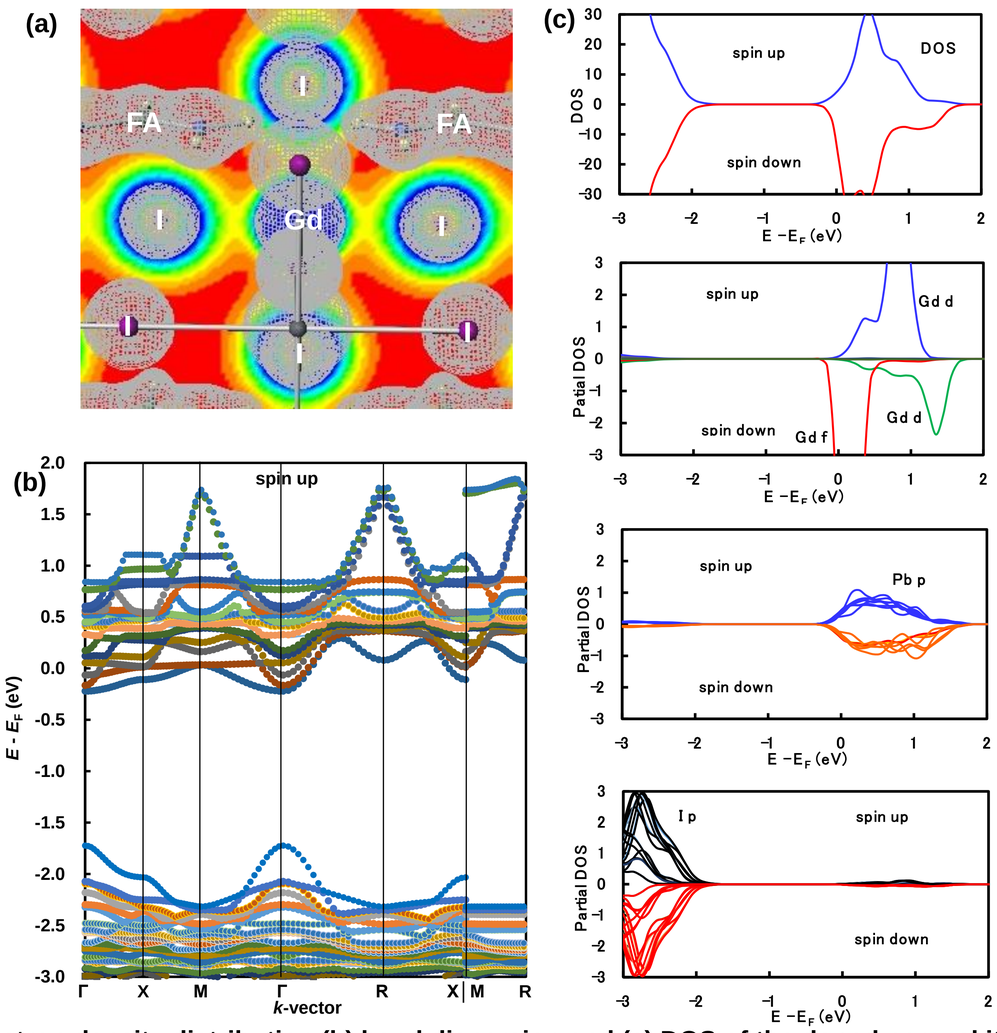
Electronic structure of Gd-doped $FAPbI_3$ perovskite crystal



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

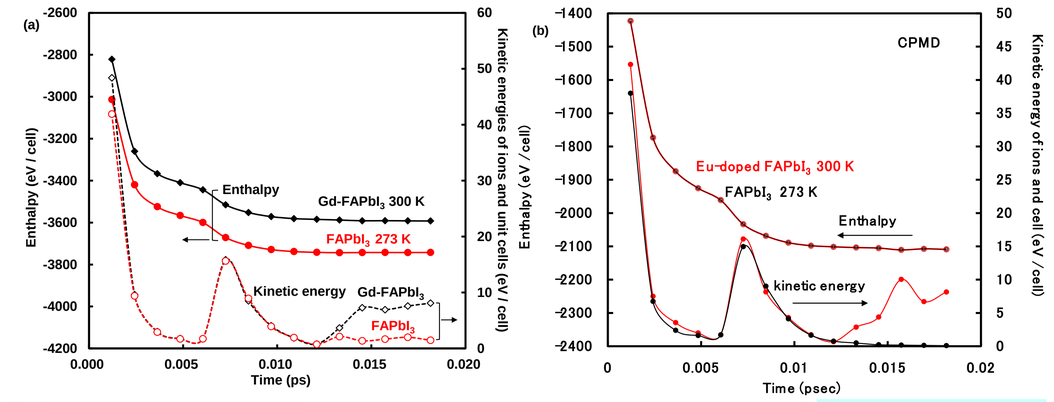
Gd: $4f^7$ $5d$

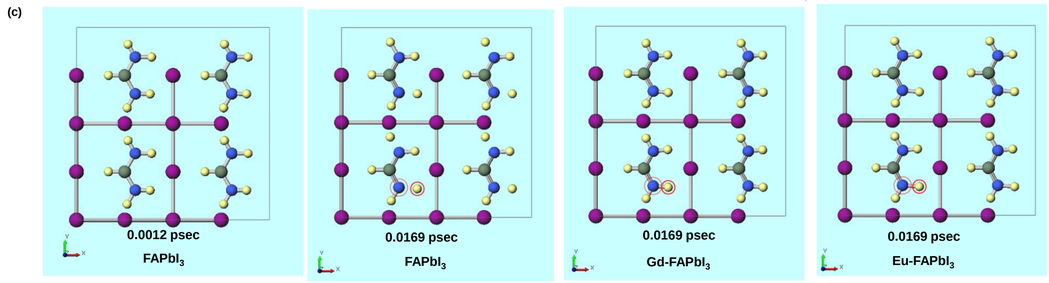
Electron density distribution of the Gd-doped $FAPbI_3$ crystal. horizontal cross-section images



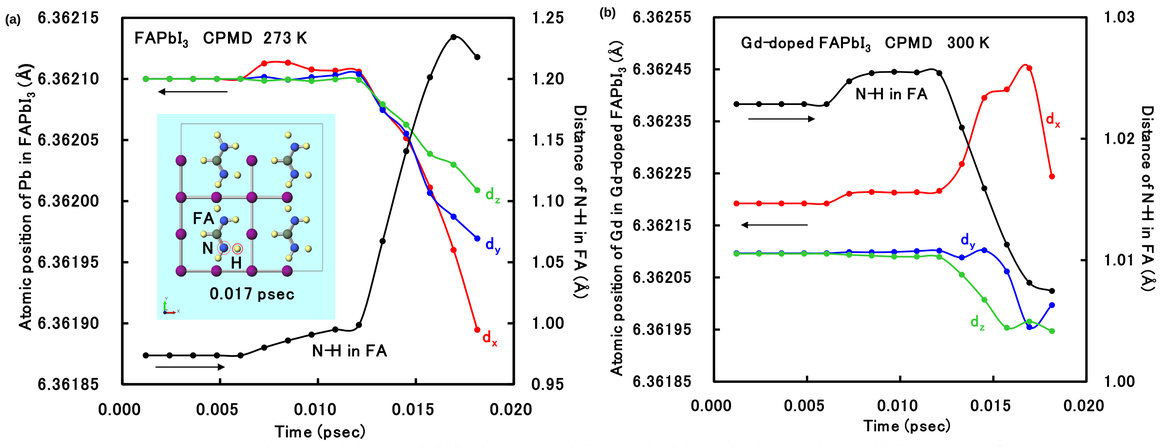
(a) Electron density distribution (b) band dispersion and (c) DOS of the doped perovskite crystal.

Thermodynamic behavior of the Ln-doped perovskite crystal





Enthalpy, kinetic energy and molecular dynamics of Gd, Eu-doped $FAPbI_3$ perovskite crystals.



Atomic position of (a) the $FAPbI_3$ and (b) Gd-doped $FAPbI_3$ crystals.

Diffusion coefficient of ions in $FAPbI_3$ crystal with defect (BOMD).

D (cm^2/s)	$FAPbI_3$	V_{Pb}-$FAPbI_3$	V_I-$FAPbI_3$	V_{FA}-$FAPbI_3$
I	8.64×10^{-6}	9.19×10^{-6}	1.10×10^{-5}	2.41×10^{-6}
Pb	8.60×10^{-7}	3.20×10^{-6}	3.75×10^{-6}	7.90×10^{-7}
H (FA)	4.02×10^{-4}	3.13×10^{-4}	1.97×10^{-4}	1.04×10^{-4}
temp. (K)	309	307	324	282

Conclusions

- Electronic structures and molecular dynamics of Gd-doped perovskite crystals were expected by first-principles calculation.
- Incorporation of Gd^{3+} ion promoted the charge transfer and carrier generation, expecting increase of J_{sc} related to η.
- Incorporation of Gd^{3+} ion inhibited the decomposition in the perovskite crystal, yielding stability better than the $FAPbI_3$ crystal.
- The Gd^{3+}-doped perovskite crystal have potential for application of photovoltaic devices with stability of performance.