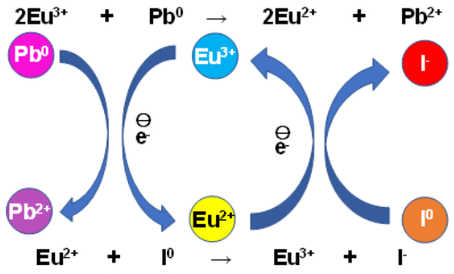
Electronic structures of Cs_3GdCl_6 and Cs_3NdCl_6 double perovskite crystals using first-principles calculations

Atsushi Suzuki, Takeo Oku, The University of Shiga Prefecture, Japan

INTRODUCTION

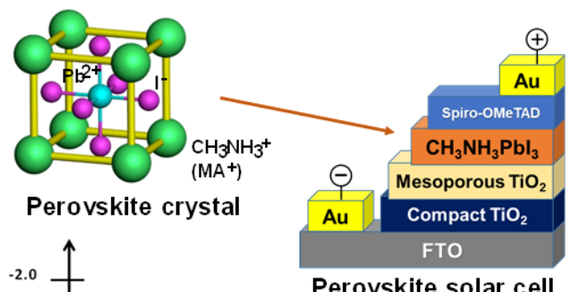
Perovskite solar cell

- 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



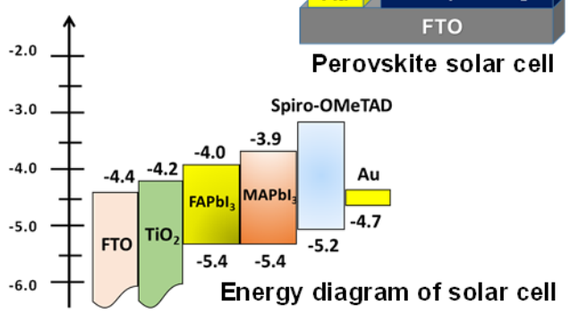
Eu^{3+}-Eu^{2+} Redox reaction

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)

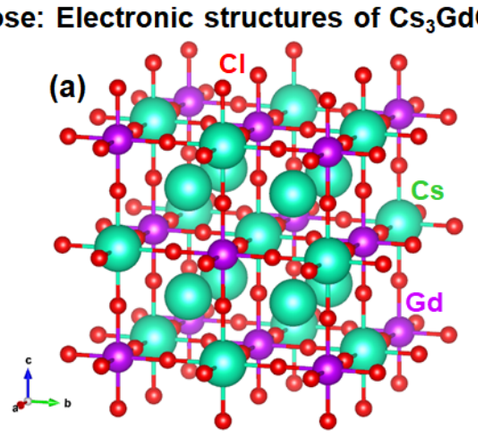
Fluorescence, Wavelength conversion, Redox reaction ⇒ photovoltaic properties Improved

Cs, Pb-free perovskite crystal

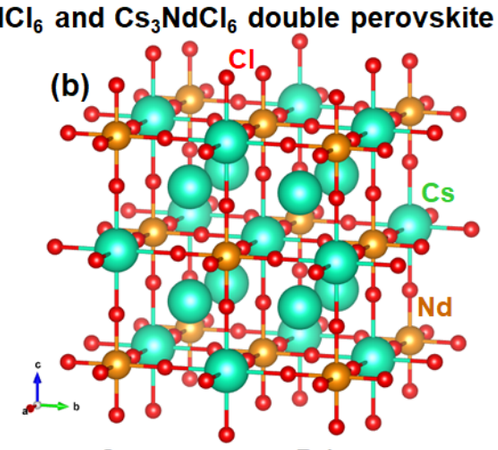
η, band gap improved

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.

Purpose: Electronic structures of Cs_3GdCl_6 and Cs_3NdCl_6 double perovskite crystals



Space group P 1
a = 10.06145 Å, b = 10.06145 Å,
c = 10.06145 Å, α, β, γ = 90.0000°

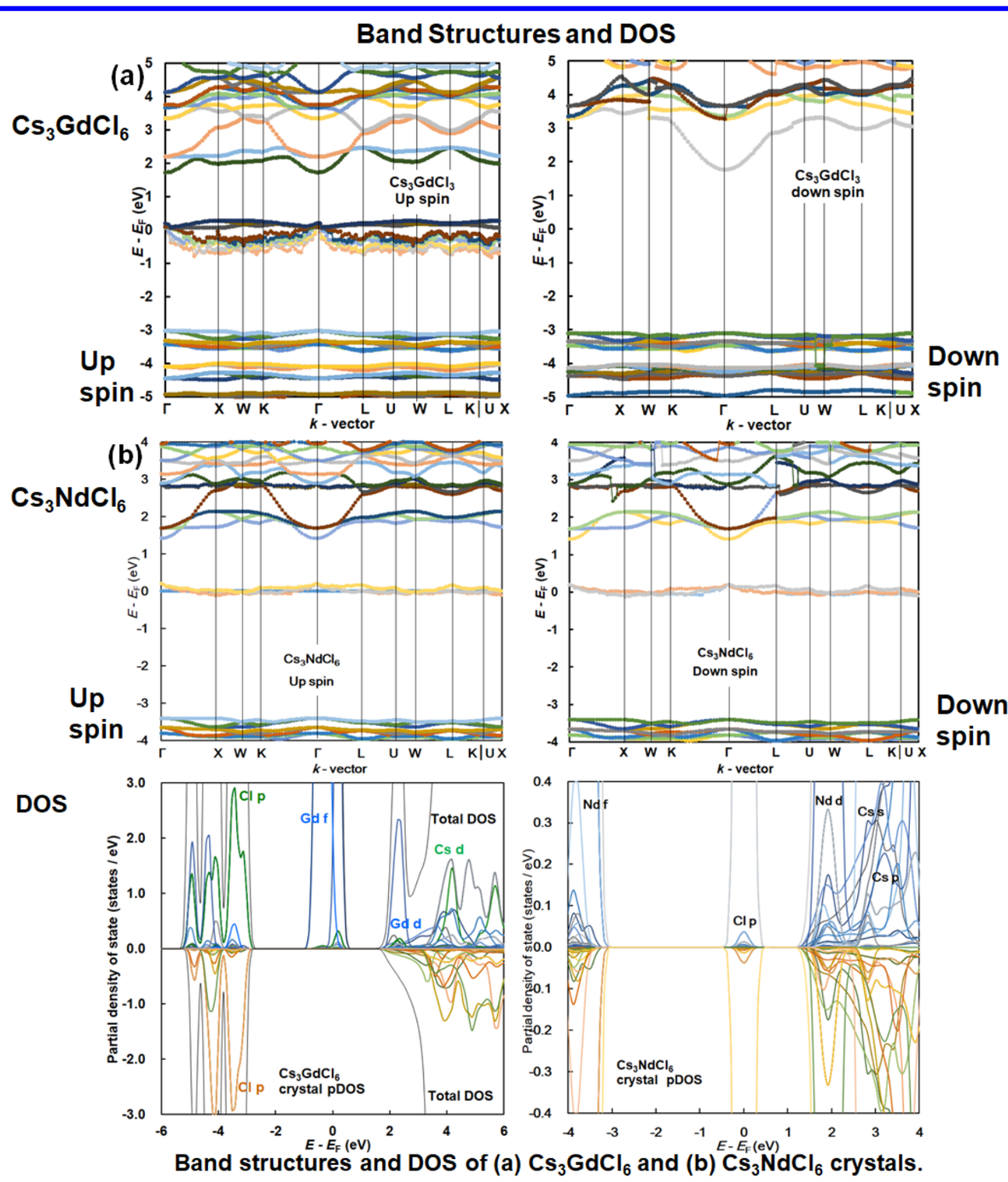


Space group P 1
a = 11.26945 Å, b = 11.26945 Å
c = 11.26945 Å, α, β, γ = 90.0000°

Optimized structures of (a) Cs_3GdCl_6 and (b) Cs_3NdCl_6 double perovskite crystals

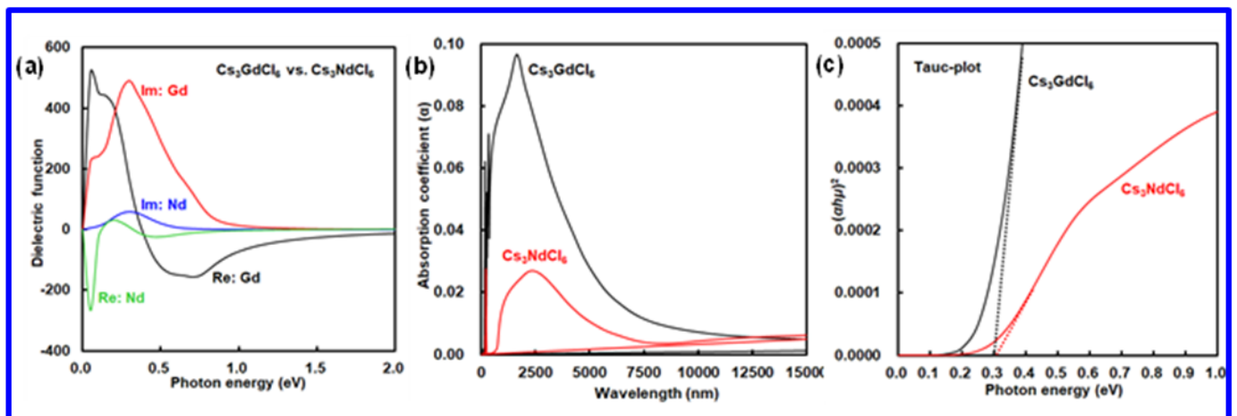
RESULTS & DISCUSSION

Band Structures and DOS

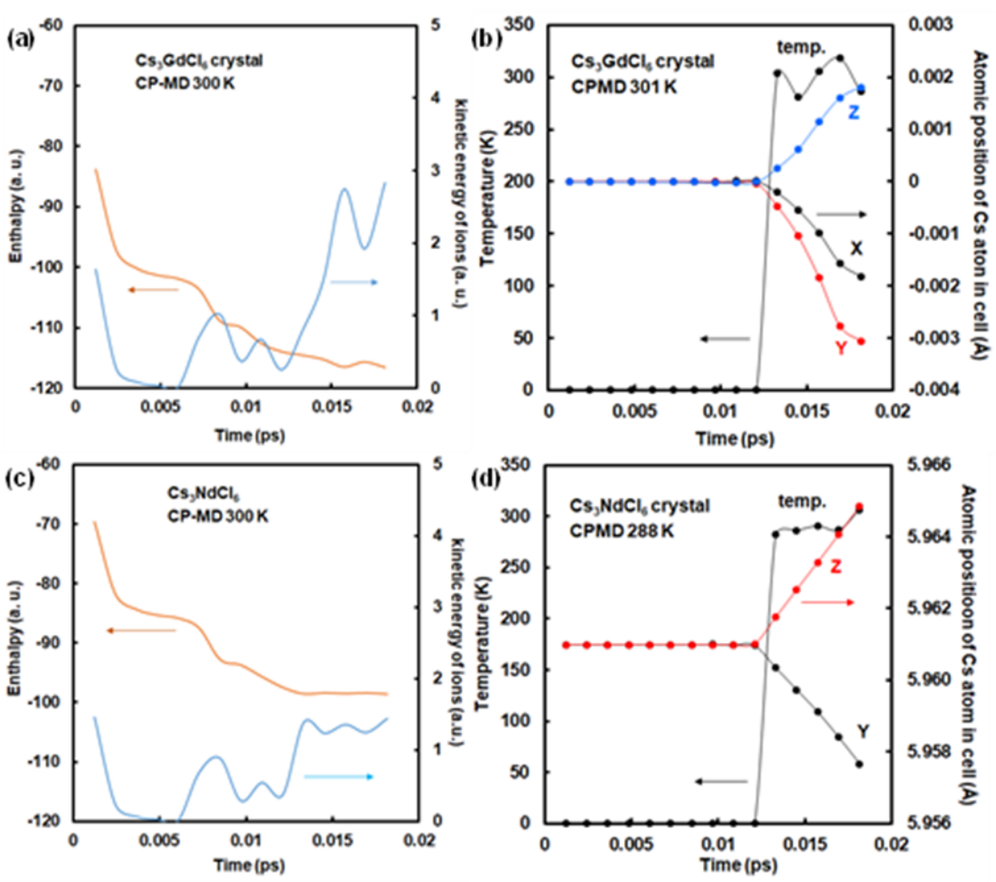


Band structures and DOS of (a) Cs_3GdCl_6 and (b) Cs_3NdCl_6 crystals.

RESULTS & DISCUSSION



(a) Real and imaginary terms of dielectronic function, (b) absorption coefficient during the wavelength and (c) Tauc-plot during photon energy of the Cs_3GdCl_6 and Cs_3NdCl_6 crystals.



Enthalpy, kinetic energy and atomic position of Cs atom in (a), (b) Cs_3GdCl_6 and (c), (d) Cs_3NdCl_6 crystals near 300 K.

Table 1 Atomic populations of 6s, 6p, 5d, 5f orbitals in Cs_3GdCl_6 and Cs_3NdCl_6 crystals.

Cs_3GdCl_6

Spin	Atomic populations of 6s, 6p, 5d, 5f orbitals on Gd^{2+} ion					Lowdin charge	Effective mass ratio	
	6s	6p	$6p_z$	$6p_x$	$6p_y$		m_e^*/m_0	m_h^*/m_0
Up	0.1949	0.2108	0.0703	0.0703	0.0703	0.3575	0.03	0.03
Down	0.1685	0.1808	0.0603	0.0603	0.0603			
	5d	$5dz^2$	5dxz	5dyz	$5dx^2$-dy^2	5dxy		
Up	1.3122	0.3479	0.2055	0.2055	0.3479	0.2055		
Down	0.6385	0.1992	0.0800	0.0800	0.1992	0.0800		
	4f	$4fz^3$	$4fxz^2$	$4fyz^2$	$4fzx^2$-zy^2	4fxyz	$4fx^3$-$3xy^2$	$4f\ 3yx^2$-y^3
Up	6.9234	0.9875	0.9885	0.9885	0.9891	0.9936	0.9881	0.9881
Down	0.0116	0.0030	0.0017	0.0017	0.0009	0.0000	0.0022	0.0022

Cs_3NdCl_6

Spin	Atomic populations of 6s, 6p, 5d, 5f orbitals on Nd^{3+} ion					Lowdin charge	Effective mass ratio	
	6s	6p	$6p_z$	$6p_x$	$6p_y$		m_e^*/m_0	m_h^*/m_0
Up	0.1582	0.1437	0.0479	0.0479	0.0479	1.4929	0.03	0.02
Down	0.1582	0.1437	0.0479	0.0479	0.0479			
	5d	$5dz^2$	5dxz	5dyz	$5dx^2$-y^2	5dxy		
Up	0.3475	0.1206	0.0355	0.0355	0.1206	0.0355		
Down	0.3475	0.1206	0.0355	0.0355	0.1206	0.0355		
	4f	$4fz^3$	$4fxz^2$	$4fyz^2$	$4fzx^2$-zy^2	4fxyz	$4fx^3$-$3xy^2$	$f\ 3yx^2$-y^3
Up	1.6034	0.0282	0.3270	0.3270	0.5063	0.0000	0.2075	0.2075
Down	1.6049	0.0282	0.3273	0.3273	0.5068	0.0000	0.2076	0.2076

CONCLUSION

- ☐ The hybridization of 5d orbital of Gd^{3+}, Nd^{3+} ion, and 6s orbital of Cs^+ ion near CB state supported charge transfer, and affected the curvature of the band dispersion and m_e^*/m_0, expecting increase of electron mobility.
- ☐ The enthalpy of the crystals suggests the crystal formation. With amount of kinetic energy, the carrier diffusion expected to be maintained while suppressing the carrier scattering with molecular dynamics.
- ☐ The Cs_3GdCl_6 crystal have high potential to apply the photovoltaic devices and optical application in the range of UV-vis-NIR.

ACKNOWLEDGMENTS

This research was funded by JSPS KAKENHI, grant number JP21K05261.

REFERENCE

Li, X.; Wang, D.; Zhong, Y.; Jiang, F.; Zhao, D.; Sun, S.; Lu, P.; Lu, M.; Wang, Z.; Wu, Z.; Gao, Y.; Zhang, Y.; Yu, W.W.; Bai, X.; *Adv. Sci.* **2023**, 10, 2207571