DFT Based First principles calculation of Lead-free $CsSnCl_3$ Perovskite: A "GGA+U" Approach

Md. Shahjahan Ali, Yasir Fatha Abed, Subrata Das, M. A. Basith

Nanotechnology Research Laboratory, Department of Physics, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh.
E-mail: m.shahjahan.ali93@gmail.com

Introduction

- **Metal halide perovskite contains chemical structure ABX_3 (where, A and B are metal cations, and X is halogen anion) [1]. It may be thought of as a big molecular atoms at the center while the corners are filled by atoms A and the sides are occupied by a smaller, negatively charged halogen atom [2] .**
- **In this investigation, we have calculated the structural properties, optical absorption, electronic band structure, charge carrier effective masses, electron charge density etc. of $CsSnCl_3$ nanocrystals within the generalized gradient approximation (GGA) and GGA+U methods.**

Theoretical Method

- The DFT based first-principles calculation was carried out using the Cambridge Serial Total Energy Package (CASTEP).
- We used both the conventional generalized gradient approximation (GGA) and the GGA+U techniques based on the PBE gradient corrected exchange-correlation functional. In GGA+U method the Hubbard U_{eff} correction is implemented in a form of $U_{eff} = U - J$, where the effects of the on-site Coulomb and exchange interaction are denoted by U and J, respectively.
- We observed that, the optimized cut-off energy of 600 eV and k-points 15 x 15 x 15 is sufficient to obtain the ground state energy of $CsSnCl_3$ perovskite.

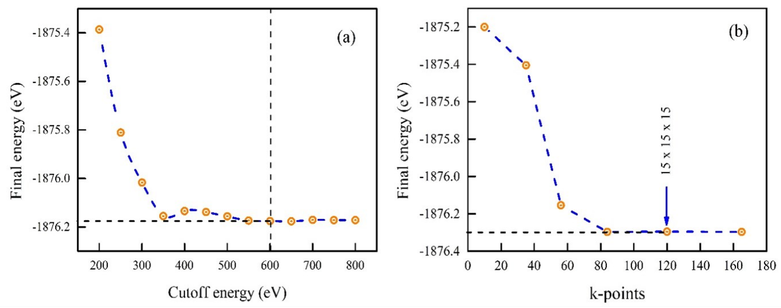
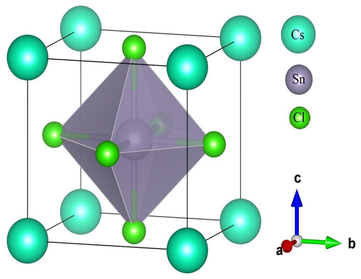


Fig.1 : (a) Plane-wave cutoff energy convergence (b) k-points grid variation for structure optimization of $CsSnCl_3$

Structural Properties



cubic crystal phase (*Pm3m space group)*

Fig.2 : Crystal structure of $CsSnCl_3$

Table 1 : The lattice parameters, unit cell volume, and bond length of $CsSnCl_3$ were calculated using first-principles methods and compared to the corresponding experimental results.

	Experimental value	U_{eff} = 0 eV	U_{eff} = 1 eV	U_{eff} = 2 eV	U_{eff} = 3 eV	U_{eff} = 4 eV	U_{eff} = 5 eV	U_{eff} = 6 eV	U_{eff} = 7 eV
$a = b = c$ (Å)	5.583	5.613	5.605	5.605	5.605	5.625	5.739	5.890	6.348
Volume (Å^3)	174.02	176.84	175.89	175.89	175.89	177.97	189.02	204.33	255.80

Optical Band Gap

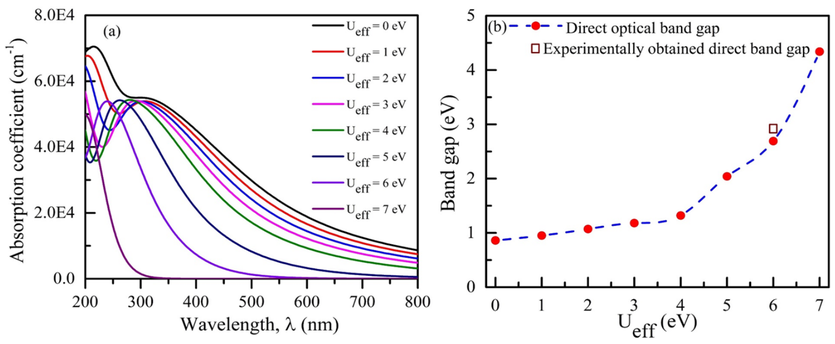


Fig.3 : (a) Absorption coefficient variation as a function of wavelength for various U_{eff}. (b) Direct optical band gap as a function U_{eff}. For U_{eff} = 6 eV the theoretically calculated direct optical band gap matches well with the experimentally obtained direct band gap of 2.98 eV (square marked).

Effective Mass

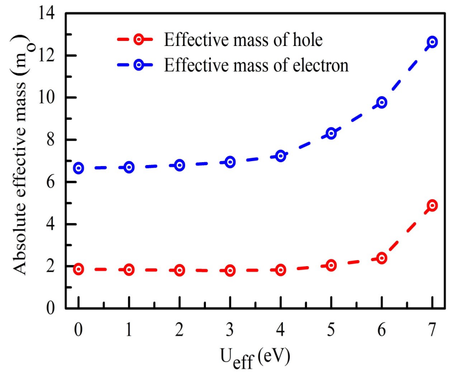


Fig.4 : Variation of the absolute effective masses of holes and electrons in terms of the electron rest mass, m_o with the increase of U_{eff} values.

- The charge carrier effective mass can be calculated using this equation [3].

$$m^* = \hbar^2 \left(\frac{d^2E}{dK^2}\right)^{-1}$$

- Generally, a semiconductor's reduced effective mass leads in increased transportability of photogenerated charge carriers from its bulk to surface, which may reduce e^--h^+ pair recombination and thus enhance photocatalytic activity. The recombination rate calculated by [3].

$$D = \frac{m_h^*}{m_e^*}$$

- The calculated "D" value is much smaller than one thus we can expect good photocatalytic performance for the material.

Density of States

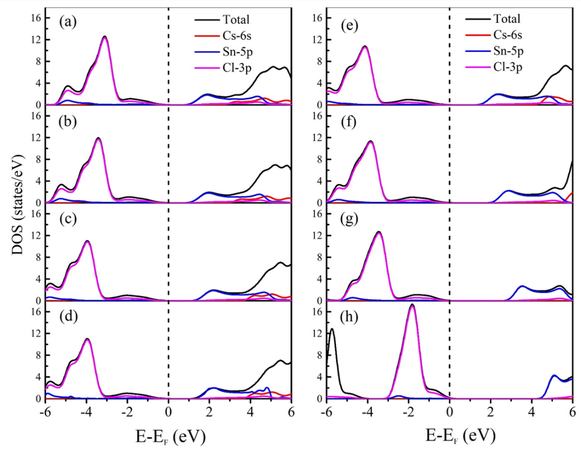


Fig.5 : The calculated total density of states (TDOS) of $CsSnCl_3$ and the Cs 6s, Sn 5p and Cl 3p orbitals.

- The valence and conduction bands are formed via the hybridization of the Cl 3p and Sn 5p and Sn 5p and Cs 6s orbitals, respectively.

Electron Charge Density

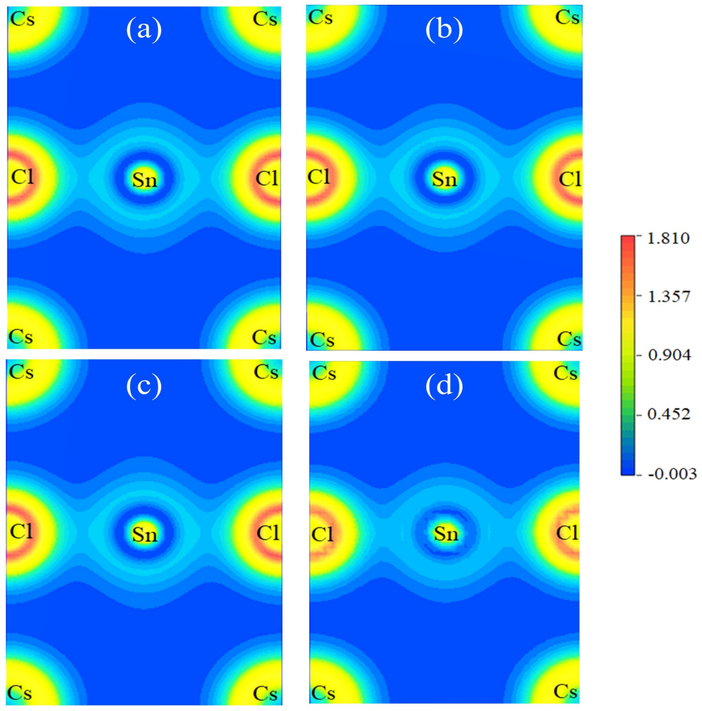


Fig.6 : Electronic charge density along (110) plane of $CsSnCl_3$ for (a) U_{eff} = 0 eV, (b) U_{eff} = 3 eV, (c) U_{eff} = 6 eV, and (d) U_{eff} = 7 eV

- The covalent type band formed in Sn and Cl atoms, while Cs atoms make an ionic bond.

Mulliken Population Analysis

Table 2: Mulliken effective charges of individual atoms, bond populations and bond lengths of $CsSnCl_3$ for different values of U_{eff} obtained via Mulliken population analysis.

Atom	U_{eff} = 0 eV	U_{eff} = 1 eV	U_{eff} = 2 eV	U_{eff} = 3 eV	U_{eff} = 4 eV	U_{eff} = 5 eV	U_{eff} = 6 eV	U_{eff} = 7 eV
				Mulliken effective charge				
Cs	0.90	0.90	0.89	0.89	0.89	0.92	0.96	0.97
Sn	0.76	0.81	0.91	0.91	0.97	1.08	1.23	1.58
Cl	-0.55	-0.57	-0.60	-0.60	-0.62	-0.67	-0.73	-0.85
Bond				Bond population				
Sn-Cl	0.35	0.34	0.33	0.33	0.32	0.32	0.31	0.22
Bond				Bond length (Å)				
Sn-Cl	2.806	2.802	2.802	2.802	2.812	2.869	2.945	3.173

- The bond population decreased with increasing U_{eff} which is indicate for the influence of Coulomb repulsion to reduce the bond covalency.

Conclusions

- Our theoretical calculation demonstrated a 90% accurate estimation of the previously reported experimentally observed optical band gap when Ueff = 6 eV was considered in the "GGA+U" method
- As the calculated "D" value much smaller than one, we predict that good photocatalytic activity for this material.
- The hybridization of Cl 3p and Sn 5p orbitals with a major contribution from Cl 3p states contributed to the formation of the valence band while the Sn 5p orbital with a minor contribution from Cs 6s orbital contributed to the creation of the conduction band of the $CsSnCl_3$.
- The concentrated overlapping electron cloud between Sn and Cl atoms demonstrates that a sigma-type covalent bond prevails between the Sn and Cl atoms, and the degree of the bond covalency reduces when a strong on-site coulomb interaction is considered.

References

[1] Hao, Feng, et al. "Lead-free solid-state organic–inorganic halide perovskite solar cells." *Nature photonics 8.6 (2014): 489-494.*
[2] Chen, Lin-Jer, et al. "Synthesis and optical properties of lead-free cesium tin halide perovskite quantum rods with high-performance solar cell application." *The journal of physical chemistry letters 7.24 (2016): 5028-5035.*
[3] Yu, Zhuo-Liang, et al. "Surface termination a key factor to influence electronic and optical properties of $CsSnI_3$." *The Journal of Physical Chemistry C 122.17 (2018): 9275-9282.*