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Abstract. A Study of The $CsPbI_3$ Two-Phase Electronic Structure Has Been Made Through Calculations Using the Density Functional Theory Method. Perovskite metal halide is used as a light-absorbing material on solar cells. This material has a high level of stability and an easy fabrication process. Also, the conversion efficiency has reached 10.1%. The two crystalline phases used are the cubic phase and the tetragonal phase. The electronic structure discussed includes the ribbon electronic curve, as well as the DOS (Density of States) curve, PDOS (Projected Density of States) curve. To find out the electronic structure, and optimization calculation is performed, namely variations in lattice constants, k-points, and cut-off energy. This optimization is done to get the structure with a minimum total energy so that its stability can be achieved. It is known that the bandgap energy value of the $CsPbI_3$ cubic is 1.44eV on the electronic and DOS curve curves. Whereas the band gap energy value of tetragonal $CsPbI_3$ is 0.6 eV on the electronic band curve and DOS as well. This shows that $CsPbI_3$ can be used for the perovskite semiconductor material.

1. Introduction

Material with perovskite structure attract attention of scientists. In this DSSC solar cell, the liquid electrolyte is vulnerable to leak so that this solar cell is not efficient instability [1]. Then carried out the development of solid state-based solar cells as one solution. Perovskite solar cells are a type of solar cell that includes perovskite structured compounds, the most common of which are hybrid inorganic or inorganic lead-based materials, as active light-producing layers. The development of energy efficiency conversion of hybrid halide perovskite solar cells has shown a significant development more than times from its initial appearance in 2009. Currently, the only problem is the field of perovskite research is the stability of the device during its operation. Another problem that must be dealt with fully is the use of lead (Pb) in perovskite compounds. Even though it is used in much smaller amounts than those in lead or cadmium based batteries, the presence of lead in products for commercial use is a problem [2].

Solar cells using $CsPbI_3$ produce Power Conversion Efficiency (PCE) from 5.95% to 10.5%. This inorganic perovskite halide is considered easier to prepare, although its efficiency is lower than hybrid solar cells. Also, $CsPbI_3$ has a high stability of up to 60 days [3]. $CsPbI_3$ had been used as photoconductive material back to 1958, but it was not used for PVs application until 2015 [4]. Hirotsu reported that the stability of the tetragonal structure did not seem long lasting, because the transition to

an ideal cubic structure was reported on heating above 47oC [5]. In 2019 the efficiency of $CsPbI_3$ is 0.74% for the tetragonal phase and 6.9% for the cubic phase this was agreed by Murugadoss [6]. The highly stable PTABr treated CsPbI3 based perovskite solar cells exhibit a reproducible photovoltaic performance with a champion efficiency up to 17.06% and stable output of 16.3% [7]. Snaith and his coworkers reported the first $CsPbI_3$ PSCs exhibiting 2.3% efficiency by adopting a planar device configuration [8]. Luo reported a modified HI additive method to prepare black-phase $CsPbI_3$, in which the as-prepared film was first immersed into hot IPA solution and then annealed at 100 °C. The efficiency of this modified $_{CsPbI3}$ PSCs reaches 4.13% [9].

One of the software is based on Density Functional Theory (DFT), Plane-wave or plane wave, and Pesudopotential (PP) namely Quantum Espresso is an electronic structure calculation tool for a system/material model. The advantage of QE is that DFT bases do not directly solve quantum mechanics so that calculations will be more efficient, PW bases that allow a large system to be represented on a small system (utilizing the periodic nature of field waves) so that calculations will be faster, and pseudopotential bases are not including calculations of the atomic nucleus potential energy but the atomic shell only to enable faster calculations [10].

2. Methods

This research is a simulation study using Quantum Espresso (QE) software. Then, do some research optimization. First, the lattice constant optimization is by making the initial lattice constant (a0) smaller than the reference value, then calculating the total energy (E0). From the first calculation you will get a relaxation structure with new lattice constants (a1) and new total energy (E1), then iterated through the comparison of En and En-1 values, if En> En-1, the condition when En-1 is expressed as optimal conditions then the value represents the optimal lattice constant. Second, K-point optimization. Calculation of total density and energy involves the wavenumber k. In principle, unlimited k is needed, but in practice, a lot of k will take a lot of calculation time. The sum in the limited Brillouin Zone (BZ) sampling is adjusted to the structure of the material band. This research uses Monkhorst-Pack mesh variation *k1xk2xk3* from *3x3x3* to *7x7x7* and seen the convergence and total energy. The third optimization is ecutwfc and ecuthro optimization. Ecutwfc is the cut-off energy for the wave function while ecuthro is the cut-off kinetic energy for the charge density. Generally, the ecuthro value is 4x the ecutwfc value. In this study, variations were made for ecutwfc from 30 to 70 Rydberg.

3. Results and discussion

3.1. $CsPbI_3$ perovskite cubic-phase

Determination of the optimum lattice constant is obtained by looking at the results that show convergent values by producing minimum total energy. The minimum total energy indicates the state of the material in equilibrium. Then the structure that produces the minimum total energy has the most equilibrium state. The results of the optimization of the lattice parameters are used to calculate the electronic structure. To see changes in the input file lattice constants and the output file of the calculation entered into the XcrysDen software.

Table 1. Grid lattice calculation.

a (Angstrom)	a relaxation (Angstrom)	Total Energy (eV)	Fermi Energy (eV)
4.3	6.33	-57763.10	3.28
6.33	6.38	-57763.18	3.06
6.38	6.38	-57763.18	3.08
6.38	6.38	-57763.18	3.08

Then in Table.1, the initial lattice constant is 4.3 angstroms. Then the vc-relax calculation is enlarged to 6.33 angstrom. In this calculation, the optimum lattice is 6.38 angstroms because when entering the lattice value of 6.38 Angstrom in the input file the value that comes out in the output file remains 6.38 Angstrom. This grid produces a total energy of -57763.18 eV.

Table 2. K-Point calculation.

K-Point	Total Energy (eV)	Fermi Energy(eV)
3x3x3	-57764.33	4.68
4x4x4	-57762.71	3.54
5x5x5	-57763.18	3.08
6x6x6	-57763.03	3.51
7x7x7	-57763.08	3.11

It can be seen in Table 2 that the total energy value of the k-point from *5x5x5* to *7x7x7* shows a stable number. So for the calculation of the dispersion curve, *5x5x5* k-point is used. Then, the cut-off energy optimization is performed to provide a limit on the amount of energy from the wave function used. These waves can be presented as a grid in the field k. The bigger the grid will make the calculation more thorough but the time required is even longer. Therefore, the cut-off energy is limited. In this calculation, the cut-off energy values are used ranging from 30 to 70. In Table 3 it can be seen that when the cut-off energy is 50 the total energy value is stable.

Table 3. Cut-off energy calculation.

Ecutwfc (Ry)	Ecuthro (Ry)	Total Energy(eV)	Fermi Energy(eV)
30	240	-57762.95	3.61
40	320	-57763.01	3.60
50	400	-57763.07	3.60
60	480	-57763.08	3.60
70	60	-57763.10	3.50

From the electronic band structure shown in Figure 1, the left side shows the electronic band structure while the right shows the Density Of States (DOS). The electronic band structure is an energy curve towards the wavefield k which shows the range of energy that is permissible as well as those that do not allow the wave function. The valence band is a band that is filled with electrons. In Figure 1, the valence band is below the Fermi energy (Ef), while the conduction band is above the Fermi energy. The value of the bandgap energy (eg) produced is 1.44eV.

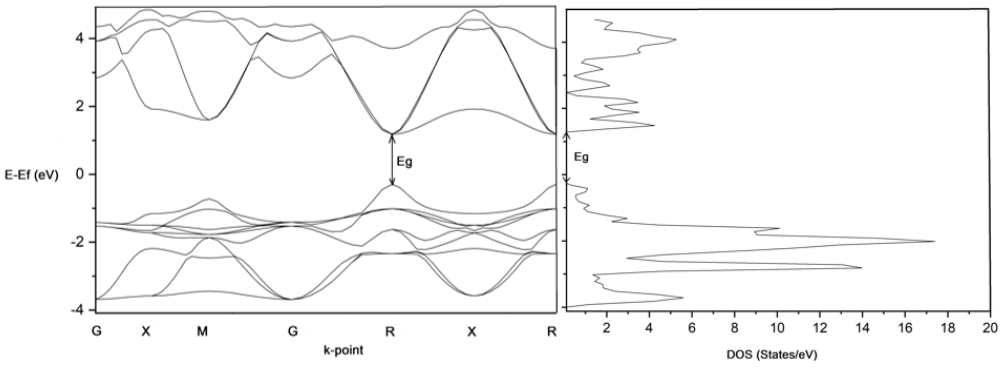

Figure 1. Electronic band structure and DOS of cubic $CsPbI_3$.

The Density Of States (DOS) curve shown in Figure 1 on the right is the total density of electrons without being known which electrons play a role in forming these states. To get this information a Projected Density of States (PDOS) calculation is performed.

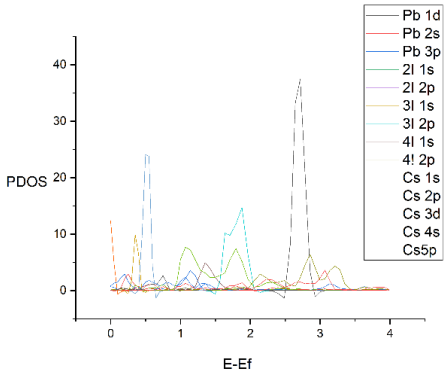

Figure 2. PDOS Structure of cubic $CsPbI_3$.

The PDOS curve of the cubic phase $CsPbI_3$ consists of Pb-1d, Pb-2s, Pb-3p, I-1s, I-2s, I-2s, I-2p, I-2s, I-2p, Cs-1s, Cs -2p, Cs-3d, Cs-4s, Cs-5p. All of these orbitals, those in the dominant band are Pb-2s and I-1s. Whereas the dominant conduction band is filled with I-2p.

3.2. $CsPbI_3$ perovskite tetragonal-phase

Based on Figure 3, it can be seen the compatibility between the electronic band curve and DOS. This shows that the calculations performed are appropriate. From the electronic band curve, it can be seen the gap energy value for tetragonal structure of 0.6 eV. For tetragonal structures, it is also known that the physical energy is 4.34 eV and the total energy is -10656.43 eV

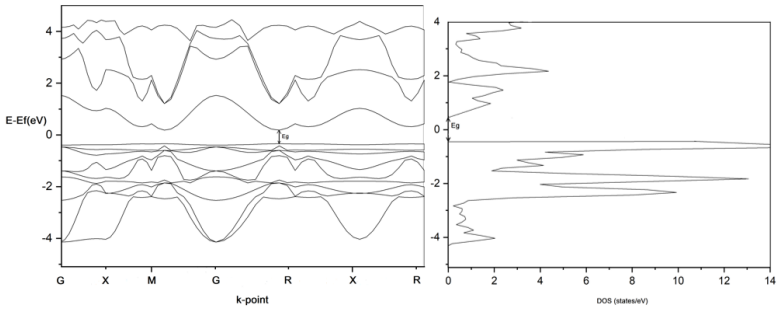

Figure 3. Electronic band structure and DOS of tetragonal $CsPbI_3$.

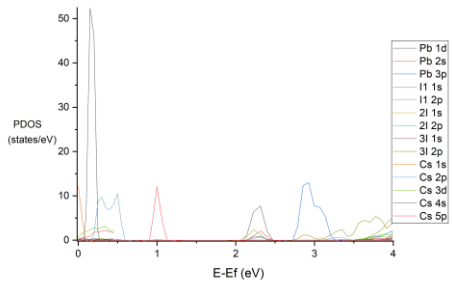

Figure 4. PDOS Structure of tetragonal $CsPbI_3$.

The PDOS curve of the tetragonal phase $CsPbI_3$ consists of Pb-1d, Pb-2s, Pb-3p, I2-1s, I2-2p, I3-1s, I3-2p, I4-1s, I4-2p, Cs-1s, Cs -2p, Cs-3d, Cs-4s, Cs-5p. Of all these orbitals, which are in the dominant valence band, are filled with Pb-1d and I3-1s. Whereas the dominant conduction band is filled by Cs-3d and Cs-2p.

4. Conclusion

The stability of the $CsPbI_3$ perovskite structure is obtained through the DFT calculation which produces the minimum total energy. Optimization of the lattice constant is done to produce the minimum total energy. The optimum lattice constant for $CsPbI_3$ is 6.38 angstroms. Based on the calculation results, the results for the bandgap value in the cubic structure are 1.44eV, whereas for the tetragonal structure is 0.6 eV. With the band gap energy value, $CsPbI_3$ cubic phase can be used as the material in solar cells because its semiconductor band gap.

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