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CALCULATION OF ELECTRONIC PROPERTIES OF $LiBX_3$ (B = Pb AND Sn; X = Br, Cl AND I) CUBIC PHASE BY DENSITY FUNCTIONAL THEORY

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ABSTRACT

Perovskite solar cells utilize perovskite as the active material to convert sunlight into electrical energy. Perovskite is a compound with a crystal structure of ABX_3, where A and B are cations, and X is an anion, usually a halide. Research continues to find perovskites with high efficiency. This efficiency is related to the electronic structure, which can be analyzed using Density Functional Theory (DFT). In this study, the electronic structure of cubic phase $LiBX_3$ perovskites (B = Pb and Sn; X = Br, Cl, and I) is investigated using Quantum ESPRESSO software. Various parameters such as cut-off energy, k-points, and lattice constants were modified to obtain optimal values. From the optimization results, the band gap, DOS, and PDOS values for the six perovskites were obtained. The resulting band gap energy (Eg) are $LiPbBr_3$ at 1,71 eV, $LiPbCl_3$ at 1,87 eV, $LiPbI_3$ at 1,43 eV, $LiSnBr_3$ at 0,51 eV, $LiSnCl_3$ at 0,65 eV, and $LiSnI_3$ at 0,28 eV. These results show that the band gap energy values increase with the change in atomic radius from Sn to Pb and decrease with the change in atomic radius from Cl, Br to I. The electronic structure calculations of $LiBX_3$ (B = Pb and Sn; X = Br, Cl, and I) show semiconductor properties that have the potential to be used as light-absorbing materials in perovskite solar cells. This study states that $LiBX_3$ has great potential in solar cell applications and offers a deep understanding of the relationship between crystal structure and its electronic properties.

Keywords: *Perovskite, DFT, Quantum ESPRESSO, Band Gap Energy*

INTRODUCTION

Solar energy is an unlimited energy resource and will always be available. This energy potential can be taken as an alternative to be converted into electrical energy using solar cells. The use of solar panels as an alternative electrical energy option can be utilised by people who need electricity supply, especially when facing constraints on the unavailability of electrical energy (Purwoto et al., 2018).

The development of solar energy technology has seen a significant increase, including the innovation of DSSC (Dye Sensitized Solar Cell) introduced by O'Regan and Grätzel in 1991. DSSCs, as third-generation photovoltaic devices, offer various advantages such as low cost, ease of fabrication, production flexibility, and high performance. This makes them a potential alternative to conventional silicon solar cells. The advantages of DSSCs attract the attention of researchers, who have increased the PCE (Power Conversion Efficiency) from 7.1% to 14.7% (Nursam & Oktaviana, 2020).

The latest generation of solar cells, which is a development of DSSCs, is PSCs (Perovskite Solar Cells). In recent years, PSCs have achieved PCE levels of up to 23.3% (Herna et al., 2022). Hybrid halide perovskites are organic and inorganic compounds with the general formula ABX3. This ABX3 crystal structure consists of two A and B cations with very different sizes and three X anions bound to the A and B cations (Wardana, 2022).

A calculation method known as TFK (Density Functional Theory) is used to calculate lattice constants, electronic properties, and optical properties of materials. The first scientists to develop the TFK method were Hohenberg and Kohn through two theorems. Firstly, they showed the interaction between electrons by using the electronic density of states. Later, Kohn and Sham developed TFK to produce the Kohn-Sham equation. (Sidik, 2022).

To obtain information about the electronic structure of $LiBX_3$ (B = Pb and Sn; X = Br, Cl and I) based on the TFK method and using Quantum ESPRESSO software, researchers first need to find the optimal calculation parameters. These parameters are ecutwfc (cut-off energy), k-points, and lattice constants. Then, these values are processed by the software to determine the electronic structure of perovskite.

RESEARCH METHOD

Checking the electronic structure of LiBX3 (B = Pb and Sn; X = Br, Cl and I) using hardware in the form of a personal computer with Intel(R) Core(TM) i3-6006U CPU @ 2.00GHz 1.99 GHz, 4.00 GB RAM (3.88 GB usable), 64-bit operating system, x64-based processor. Software used: VirtualBox serves to execute the Quantum ESPRESSO operating system in the Windows operating system, Notepad++ serves as a place to write and/or edit scripts, Quantum ESPRESSO serves to process scripts that have been written in Notepad++, XcrySDen serves to visualise crystal structures, and Gnuplot serves to create band structure, DOS, and PDOS graphs. The creation of input files contains several modules that are already available in the Quantum ESPRESSO package, such as pw.x, bands.x, etc. The types of materials and their structural shapes are defined in the programme code.

The determination of the minimum value of ecutwfc refers to the pseudopotential data where the type of pseudopotential used is Semi Local Norm Conserving with Generalised Gradient Approximation Perdew Burke Enzerhof exchange correlation functional (GGA-PBE). The parameters that must be optimised to obtain accurate electronic property calculation results for LiBX3 perovskites (B = Pb and Sn; X = Br, Cl and I), namely ecutwfc, k-points, and lattice constants.

The electronic properties of LiBX3 perovskite (B = Pb and Sn; X = Br, Cl and I) can be seen in Figure 1 below.

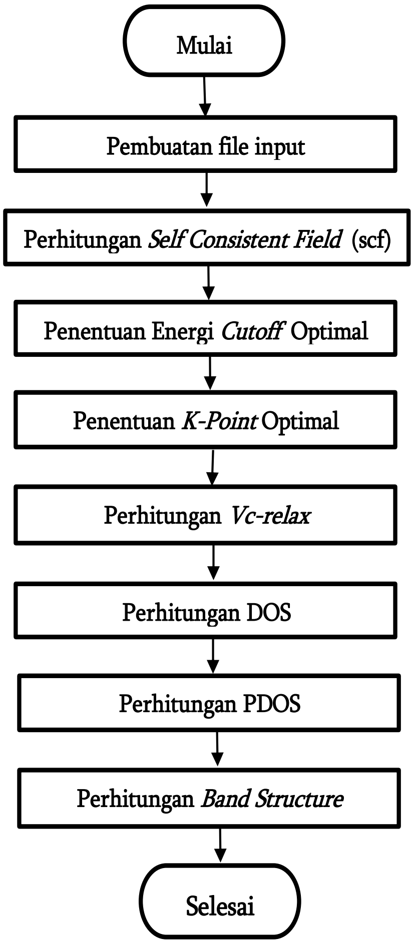


Figure 1. Research flowchart

RESULT AND DISCUSSION

1. Ecutwfc Optimisation

The calculation results of the LiPbl$_3$ ecut-off energy value can be seen in Figure 2.

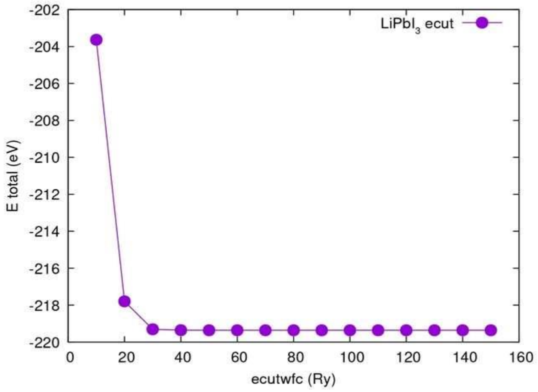


Figure 2. Calculation results of LiPbl$_3$ ecut-off energy value

The optimisation results of ecutwfc parameters for LiPbI$_3$ calculations in the range of 10-150 rydberg are shown in Figure 2. Judging from the value of 30 to 150 rydberg, the total energy value does not change significantly. Therefore, the value of 90 rydberg was chosen as ecutwfc because the researcher took a precision of 4 numbers behind the comma. Through the same method, the perovskites LiPbBr$_3$ 90 Ry, LiPbCl$_3$ 110 Ry, LiSnBr$_3$ 80 Ry, LiSnCl$_3$ 110 Ry, and LiSnl$_3$ 60 Ry were obtained. As it is known that the greater the cut-off energy value will make the calculation more precise but the time required is also longer (Pitriana et al., 2018).

2. K-points Optimisation

The calculation results of the k-point value of LiPbl3 can be seen in Figure 3.

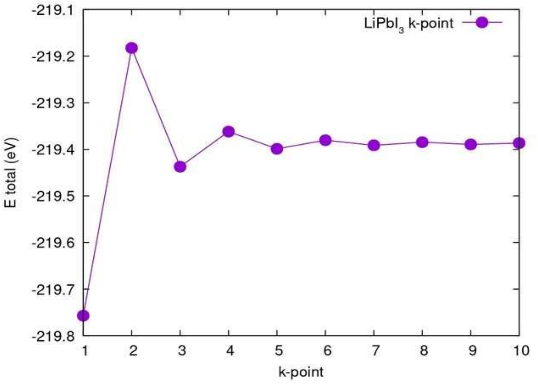


Figure 3. Calculation result of LiPbl$_3$ k-points value

The optimal k-points value is determined by inputting random numbers while ensuring that the row of numbers is the ground k-points position. The crystal structure used is cubic, while k-points have a general formula, namely n x n x n, so to determine the optimal k-points value is done by randomising numbers starting with 1 x 1 x 1 (Wahyuni, 2022).

Figure 3 shows the ratio of k-points to total energy for LiPbI$_3$. From 6 x 6 x 6 to 10 x 10 x 10, the total energy value does not change significantly. Therefore, the value of 9 x 9 x 9 was chosen as the k-points because the researcher took the precision of 2 numbers behind the comma. Through the same method, the perovskite k-points LiPbBr$_3$ 7×7×7, LiPbCl3 7×7×7, LiSnBr3 8×8×8, LiSnCl$_3$ 9×9×9, and LiSnl$_3$ 7×7×7 were obtained. As it is known that the greater the value of k-points will make the calculation more precise but the time required is also longer (Pitriana et al., 2018).

3. Lattice Constant Optimisation

The results of the calculation of the lattice constant value of LiPbl3 can be seen in Table 1.

Table 1. Calculation results of LiPbl$_3$ lattice constant value

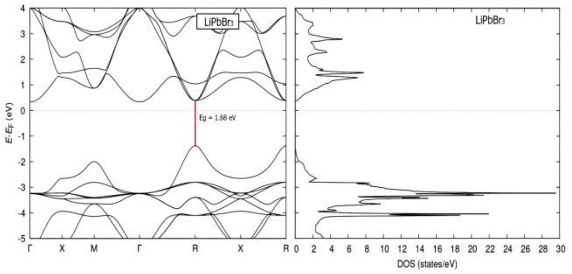
a (Å)	a relaxation (Å)	Etot (eV)
5	6,318	-220,17100591
6,318	6,321	-220,17101456
6,321	6,321	-220,17101310

The lattice constant is initially set at 5 Å. After the vc-relax calculation, the lattice constant will increase until the optimum lattice constant is obtained. Because when the optimum lattice constant value is entered into the next input file, the total energy value does not change. This is due to the enlargement of the lattice parameter value set as an initial guess in the scf input to the optimised value after the program is run (Maysari Angraini et al., 2021). Therefore, the value of 6.321 Å as the lattice constant is then used in the calculation of the electronic structure of LiPbI3. As for the perovskites LiPbBr$_3$ is 5.938 Å, LiPbCl$_3$ is 5.662 Å, LiSnBr$_3$ is 5.802 Å, LiSnCl$_3$ is 5.523 Å, and LiSnl$_3$ is 6.175 Å.

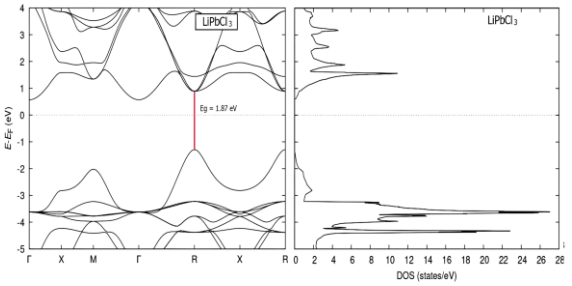
4. Band Structure and State Density

The Band Structure and Density of States graphs of LiBX3 perovskite (B = Pb and Sn; X = Br, Cl and I) can be seen in Figure 4

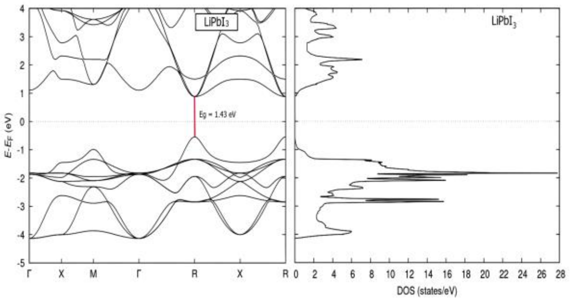
(a) $LiPbBr_3$



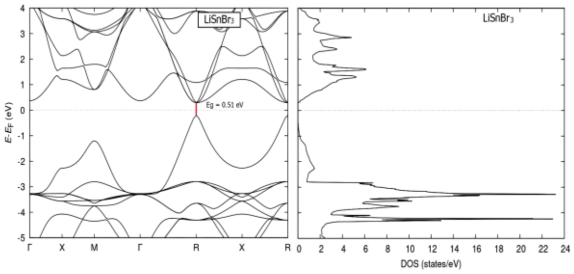
(b) $LiPbCl_3$



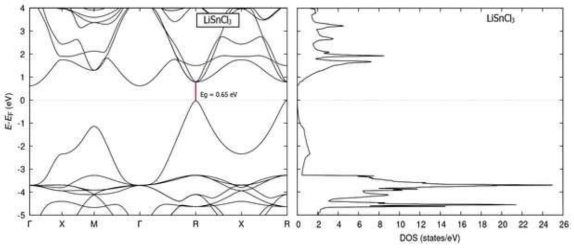
(c) $LiPbI_3$



(d) $LiSnBr_3$



(e) $LiSnCl_3$



(f) $LiSnI_3$

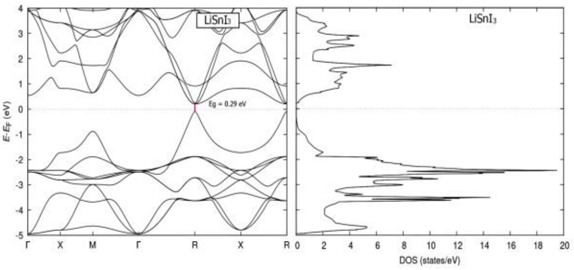


Figure 4. Band Structure and Density of States graphs of perovskite (a) $LiPbBr_3$, (b) $LiPbCl_3$, (c) $LiPbl_3$, (d) $LiSnBr_3$, (e) $LiSnCl_3$, and (f) $LiSnl_3$

Based on Figure 4, the resulting band gap energy values of $LiBX_3$ perovskites (B = Pb and Sn; X = Br, Cl and I) can be seen in Table 2

.

Table 2. Band gap energy value results of $LiBX_3$ perovskite (B = Pb and Sn; X = Br, Cl and I)

Perovskite	**Eg Research (eV)**	**Eg Referenece (eV)**
$LiPbBr_3$	1,71	1,708
$LiPbCl_3$	1,87	-
$LiPbI_3$	1,43	1,400
$LiSnBr_3$	0,51	-
$LiSnCl_3$	0,65	-
$LiSnI_3$	0,29	0,287

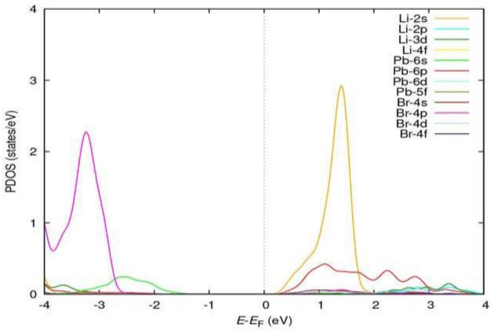
The resulting band gap energy (Eg) values for $LiPbBr_3$ are 1.71 eV, for $LiPbCl_3$ are 1.87 eV, for $LiPbI_3$ are 1.43 eV, for $LiSnBr_3$ are 0.51 eV, for $LiSnCl_3$ are 0.65 eV, and for $LiSnI_3$ are 0.29 eV. The band gap energies for these six crystal systems appear to be highly correlated with the metal cation (B) and halogen anion (X) elements. The band gaps decrease in the following order: $LiPbCl_3$, $LiPbBr_3$, $LiPbI_3$, $LiSnCl_3$, $LiSnBr_3$, and $LiSnI_3$. Compared to the computational results by Pitriana, 2019 in her dissertation, the band gap energy of the same perovskite data is very close. The study reported that the band gap energies for $LiPbBr_3$, $LiPbI_3$, and $LiSnI_3$ were 1.708 eV, 1.400 eV, and 0.287 eV, respectively. Calculation of the percentage error between the research band gap energy and the reference shows 0.117% for $LiPbBr_3$, 2.142% for $LiPbI_3$ and 1.045% for $LiSnI_3$. Thus, the researcher guarantees that the band gap energy values for other perovskites are correct.

After looking at Figure 4, it can be concluded that the value of band gap energy gets larger with the change of larger atomic radius from Sn to Pb and the value of band gap energy gets smaller with the change of larger atomic radius from Cl, Br to I. Referring to the Shockley-Queisser limit, materials having a large band gap energy of about 1.34 eV have the potential to achieve PCE levels of up to 35% in p-n junction solar cell divaises (Shockley & Queisser, 1961). Therefore, perovskites such as LiPbX3 (LiPbBr$_3$, LiPbCl$_3$, and LiPbI$_3$) have great opportunities as light-absorbing materials with high energy conversion efficiency and the closest value is LiPbI$_3$ at 1.43 eV.

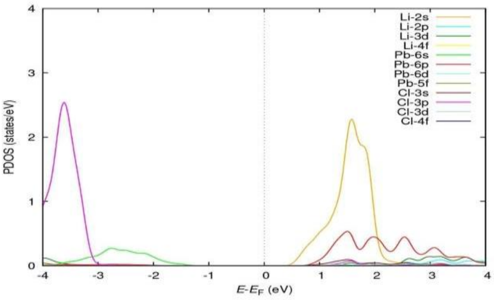
5. Projected Density of States

The results of the Projected Density of State graph of LiBX$_3$ perovskite (B = Pb and Sn; X = Br, Cl and I) can be seen in Figure 5.

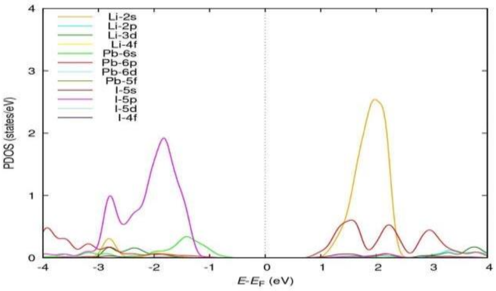
(a) LiPbBr$_3$



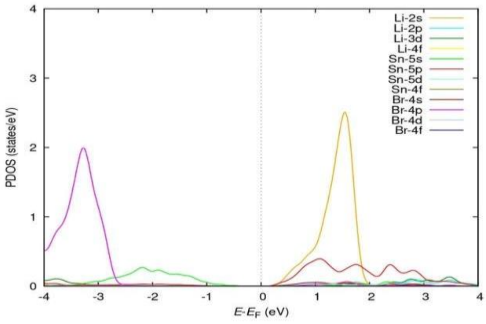
(b) LiPbCl$_3$



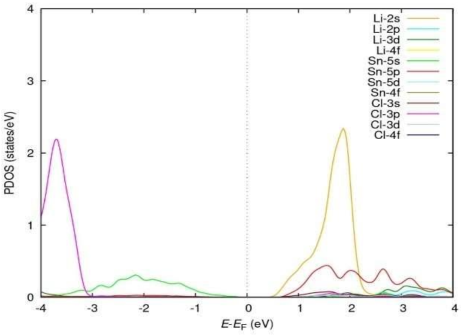
(c) LiPbI$_3$



(d) LiSnBr$_3$



(e) LiSnCl$_3$



(f) LiSnI$_3$

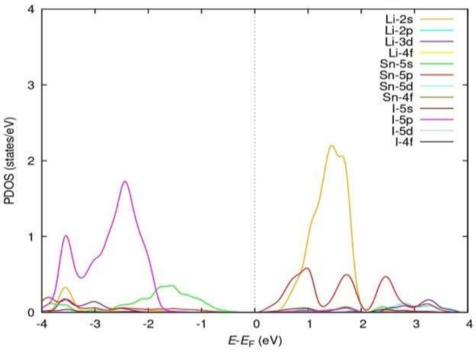


Figure 5. Projected Density of States perovskite (a) LiPbBr$_3$, (b) LiPbCl$_3$, (c) LiPbl$_3$, (d) LiSnBr$_3$, (e) LiSnCl$_3$, and (f) LiSnl$_3$

The DOS curve in Figure 5 shows the total electron density without details of the type of electrons that contribute to the formation of the state. To obtain this information, a PDOS calculation is performed. In cubic phase LiPbBr$_3$, the valence band is dominantly occupied by Br$_{4p}$ and Pb $_{6s}$ orbitals, while the conduction band is dominantly occupied by Li$_{2s}$ and Pb$_{6p}$ orbitals. In the cubic phase LiPbCl$_3$, the valence band is dominantly filled by Cl$_{3p}$ and Pb$_{6s}$ orbitals, while the conduction band is dominantly filled by Li$_{2s}$ and Pb$_{6p}$ orbitals. In the cubic phase LiPbI$_3$, the valence band is dominantly filled by I$_{5p}$ and Pb$_{6s}$ orbitals, while the conduction band is dominantly filled by Li$_{2s}$ and Pb$_{6p}$ orbitals. In the cubic phase $LiSnBr_3$, the valence band is dominantly occupied by Br_{4p} and Sn_{5s} orbitals, while the conduction band is dominantly occupied by Li_{2s} and Sn_{5p} orbitals. In the cubic phase $LiSnCl_3$, the valence band is dominantly occupied by Cl_{3p} and Sn_{5s} orbitals, while the conduction band is dominantly occupied by Li_{2s} and Sn_{5p} orbitals. Finally, in the cubic phase $LiSnI_3$, the valence band is dominantly filled by I_{5p} and Sn_{5s} orbitals, while the conduction band is dominantly filled by Li_{2s} and Sn_{5p} orbitals.

From these results it can be concluded that atoms A (Li), B (Pb or Sn), and X (Br, Cl, or I) all play a role in the formation of band gap energy. The A atom contributes to the conduction band, while the X atom contributes to the valence band. Atom B also plays a role in forming the valence band and conduction band, but with less influence. This may be caused by the position of the B atom which is at the center of the cube, so it does not change the crystal symmetry significantly.

CONCLUSION AND SUGGESTION

From the results of the calculations that have been carried out, it can be concluded that the resulting band gap energy value for $LiPbBr_3$ is 1.71 eV, $LiPbCl_3$ is 1.87 eV, $LiPbI_3$ is 1.43 eV, $LiSnBr_3$ is 0.51 eV, $LiSnCl_3$ is 0.65 eV, and $LiSnI_3$ is 0.29 eV. Referring to the Shockley-Queisser limit which states that materials that have a band gap energy of around 1.34 eV have the potential to reach PCE levels of up to 35% in p-n junction solar cell devices, then $LiPbX_3$ is the most ideal perovskite because of its band gap energy value. can be used as a light absorbing material with a high PCE and the closest value is $LiPbI_3$ of 1.43 eV.

Suggestions for future researchers are to explore the phonon, thermal and optical properties using the same perovskite, as well as varying different phases or cations and anions to obtain materials with maximum power conversion efficiency.

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