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The computation parameters optimizations for electronic structure calculation of LiPbI₃ perovskite by the density functional theory method

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Abstract. Inorganic metal halide perovskite crystals, such as $CsPbI_3$, have been extensively studied for solar cell applications due to their structural stability and high energy conversion efficiency. In this paper, we report the optimizations of computation parameters, namely the kinetic energy cut-off, k-point and lattice constant, which were used in the electronic structure calculations of $LiPbI_3$ crystal. The calculations were based on the Density Functional Theory (DFT) method using the Quantum Espresso computational package. The variable-cell relaxation algorithm (vc-relax) was employed for obtaining the lowest total energy value by using ultrasoft pseudopotentials and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functions. The optimum of kinetic energy cut-off was obtained to be 40 Rydberg, the k-point was at least of 5×5×5, and the band gap energy was 1.45 eV. The calculated electronic structure shows that LiPbI3 properties are different from CsPbI3, but it may have a semiconductor property.

1. Introduction

In order to compete with silicon-based solar cells, the new generation of solar cells should give some advantages, such as easy to be fabricated by using a low-cost and environmental friendly fabrication technology. At present, metal halide based inorganic perovskites and hybrid inorganic-organic perovskites have been developed as active materials for the new generation of solar cells. The developments of hybrid halide perovskite solar cells show a significant growth in their energy conversion efficiencies, which increased more than fivefold from the first report in 2009 [1-5]. This progress also attracts much attention for understanding the origin of efficient photovoltaic effects (PV) in these halide perovskites, which are not observed in other types of perovskite crystals.

Inorganic metal halide perovskites have been much studied so far. One of the advantages of this inorganic perovskite is its higher chemical stability in comparison to hybrid organic-inorganic perovskites. Qian et al. have calculated the electronic structure of $CsPbX_3$ (X = F, Cl, Br) and its modified structures by replacing the Cs element with organic groups [6]. The efficiency of solar cells

from CsPbBr3 and its modified structure with organic cations have been studied by Cells et al. [7]. Many researchers have also studied perovskite with iodide, as the halide element, such as Filip et al. who showed the bandgap engineering in $APbI_3$, where A denotes the alkali and organic cations [8].

In this paper, we present the computational studies on another type of inorganic metal halide perovskite, namely $LiPbI_3$. In this type of perovskite, the Li element replaces the Cs element in the most studied $CsPbI_3$ perovskite. It should be noted, however, that the Li atom size is much smaller than the Cs atom. Moreover, the number of electrons in the Li atom much smaller than that in the Cs atom. Therefore, a significant difference in their crystal structures and electronic structures may be expected. In order to get the information on the LiPbI3 electronic structures from electronic computational studies based on the density functional theory (DFT) method, it is necessary to find firstly the optimized calculation parameters. In this report, the optimization of three calculation parameters, namely the kinetic energy cut-off (ecutwfc), k-point, and lattice constant, were then used to determine the electronic structure of $LiPbI_3$ perovskite.

2. Method

The electronic structure calculations were carried out by using an open source DFT computational package, namely Quantum Espresso (QE) [9]. There are five important parts of the input file, i.e. code calculation, data structure, parameter data, k-points and pseudopotential files. The calculation code contains some modules that have already been available in the QE package, such as pw.x, bands.x etc. The types of materials and their properties are defined in the structure data. The parameter data contains quantities of constants determined by QE such as kinetic energy cut-off (ecutwfc), the k-points containing the Brillouin zone to be determined and pseudopotential files containing (pseudo) potential files from existing materials in the QE library. Those parts (except the code part) must be optimized to get accurate calculation results for this $LiPbI_3$ perovskite, namely the kinetic energy cut-off (ecutwfc), k-point, and lattice constant.

2.1. Optimization of kinetic energy cut-off, k-point and lattice constant

2.1.1. Kinetic energy cut-off (ecutwfc) optimization. The kinetic energy cut-off (ecutwfc) optimization was done to limit the number plane waves with energy smaller than and/or equal to kinetic energy cut-off. This is required to computation efficiency while maintaining the accuracy of the computation result. In a periodic system, the plane wave is expressed by [9].

$$\psi_k(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\bullet\mathbf{r}} \tag{1}$$

where G is a reciprocal lattice vector. This plane wave can be represented as a grid in the k-plane. The larger the number of grid will make the calculation to be more accurate but the required calculation time becomes longer. Therefore, it is usually limited by the cut-off energy unit, given by

$$\frac{\hbar|\mathbf{k}+\mathbf{G}|^2}{2m} \leq E_{cut} \tag{2}$$

The parameter used in the input file is ecutwfc. In this study, the ecutwfc value was varied in the range of 10-70 Rydberg.

2.1.2. The k-point optimization. The total energy and density calculations ideally are carried out for all values of **k** plane waves. However, we practically limit only for a finite number of **k** plane waves. The summation in limited Brillouin Zone (BZ) sampling was adapted where we used the Monkhorst-Pack mesh variation $k_1 \times k_2 \times k_3$ from 1×1×1 to 10×10×10 and for finding the best convergence and total energy value.

2.1.3. Lattice constant optimization. Structural optimization was done by optimizing the crystal lattice constant. In this study, the perovskite crystal structure was assumed to be a cubic crystal structure, which exists in the high-temperature region as reported elsewhere [10]. This lattice constant optimization was done by giving the initial lattice constant (a0) smaller than the expected value in the calculation of its total energy. The calculations were iterated where at the end of each step we obtained the new lattice constants (a1) and the new total energy (E1). The iteration continued until we obtained the lowest total energy.

2.2. Band structure calculation of LiPbI$_3$
The results of those parameter optimizations were used in the input file for the variable-cell relaxation (vc-relax) calculation. In calculating the total energy, the ultrasoft potential with the Rappe Rabe Kaxiras Joannopoulos (RRKJ) method and the functional type of exchange-correlation Perdew-Burke-Ernzerhof (PBE) as well as scalar relativistic type were used. One of the calculation parameters associated with the ecutwfc parameter is the ecutrho parameter which can be set to be 8 to 12 times of the ecutwfc parameter for ultrasoft pseudopotential. In this calculation, we used ecutrho = 8 × ecutwfc.

The crystal structure of LiPbI$_3$ is a cubic crystal with Li atom at each cubic corner, Pb atom at cubic center and I atom at each cubic face. The symmetry path used in the calculation of the band structure for cubic is Γ-X-M-Γ-R-X|M-R as shown in figure 1 [11].
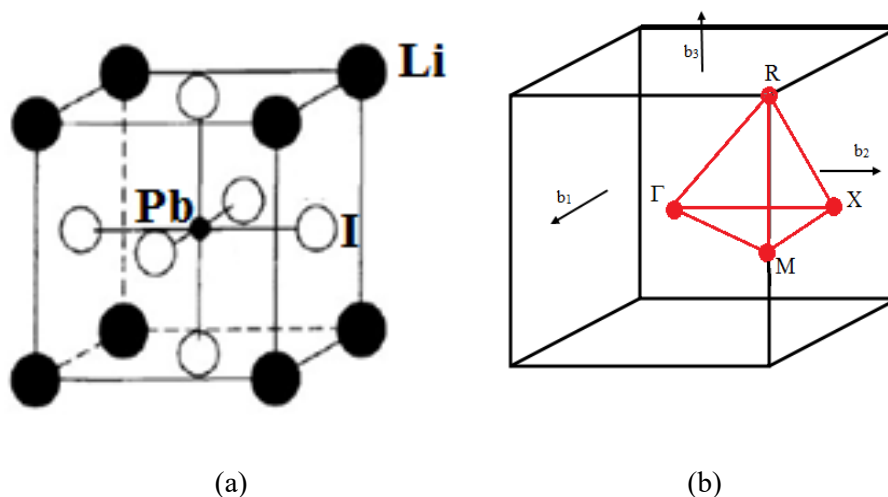

(a)   (b)

Figure 1. (a) Crystal structure of LiPbI$_3$ and (b) k-path used in the electronic structure calculation.

3. Results and discussion

3.1. Parameters calculation optimization
The optimization result of the ecutwfc parameter for this LiPbI$_3$ calculation in the range of 10-70 Rydberg is shown in figure 1. The total energy value decreases as the ecutwfc parameter increases. However, from the value of 30 to 70 Rydberg, the total energy value does not change significantly. Therefore, the value of 40 Rydberg as kinetic cut-off energy was then used in calculating the electronic structure of LiPbI$_3$.

In the optimization of k-point value, the results for grid variations from 1 to 10 are shown in the figure 2. The figure shows the total energy value generated for each grid. It appears that the lowest total energy value is generated on the grid of 1×1×1, but the value is not taken because it is the first BZ boundary and less encompasses many atoms. The total energy value fluctuates but relative constant for grid size larger than 4. Therefore, the grid size of 5×5×5 may be chosen for further calculation processes. This k-point value is precise enough to get the total energy, but it needs denser points for the calculation of electronic structure to get the more smooth curve. Here, we used k-point in 11×11×11.
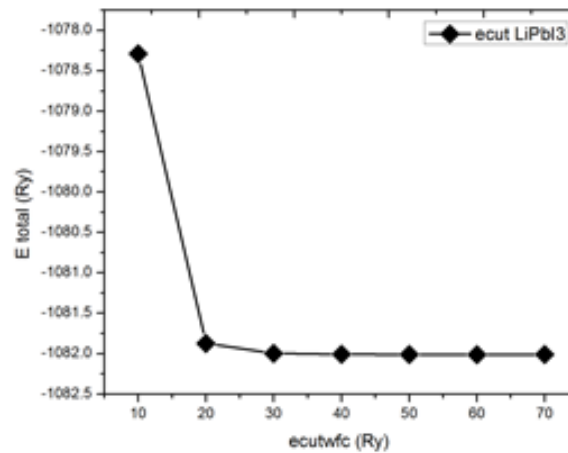
Figure 2. Kinetic energy cut-off optimization of LiPbI$_3$.

Table 1 shows the lattice constant values (a_{relax}) obtained from the calculation in comparison to their initial values (a_0). It can be seen that the third calculation with the a$_0$ = 6.3725 Å yields the total energy of E_0 = -4429.607 eV, which is the lowest among other results. The crystal structure with lattice constant a = 6.3725 Å is then considered as the most optimum structure for this LiPbI$_3$ crystal.
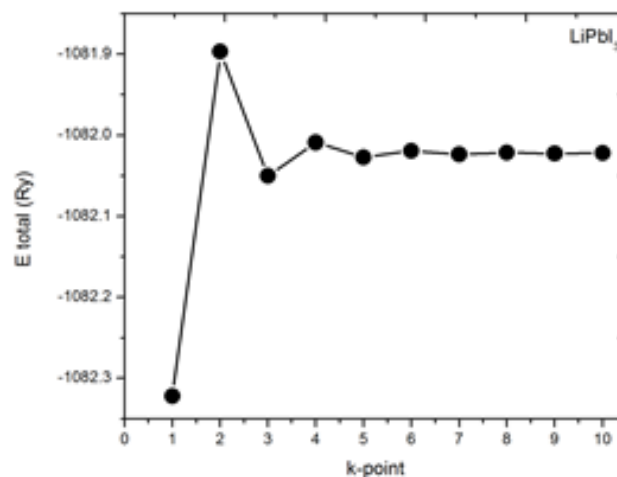

Figure 3. Kinetic energy cut-off optimization of LiPbI$_3$.

Table 1. Lattice constant optimization of LiPbI3.

Calculation	a_0 (Å)	a_{relax} (Å)	E_{tot} (eV)
1	4.3000	6.0057	-4383.524
2	6.0057	6.3725	-4429.607
3	6.3725	6.3852	-4430.069
4	7.000	6.3950	-4429.416

3.2. Band structure of LiPbI$_3$

The optimized kinetic energy cut-off, k-point, and lattice constant parameters were then used as the input parameters for the calculation of the electronic structure of LiPbI$_3$. The result is shown in figure 4. The band structure of LiPbI$_3$ shows a direct bandgap at the R symmetry point (0.5; 0.5, 0.5). The band gap energy value is calculated from the difference of the lowest energy value in the conduction band with the highest energy value in the conduction band. The band gap energy of LiPbI$_3$ is then determined

to be 1.45 eV. As a comparison, the work by Filip *et al*. gave 1.79 eV for the band gap energy of $LiPbI_3$ [8]. The difference may rely on the difference in crystal structure where they used orthorhombic crystal structure in their calculation. The comparison with the experimental results is still difficult to be done because the measurement should be done at high temperature. The work done by Dimesso *et al*. showed that the $LiPbI_3$ gap energy is about 2.36 eV at room temperature [12].
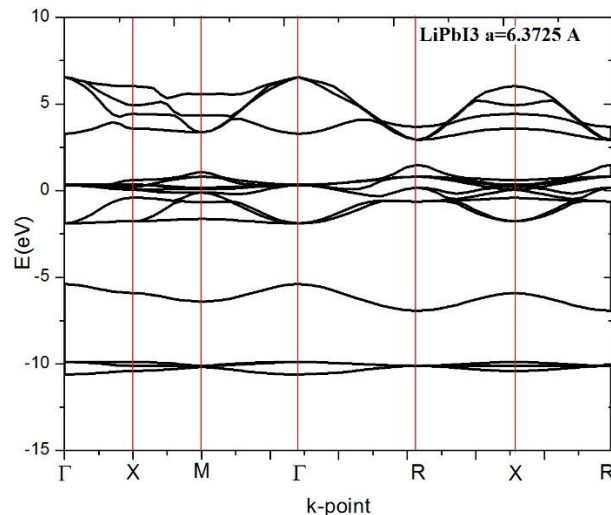

Figure 4. Band structure of $LiPbI_3$.

4. Conclusion

The optimization of computation parameters for electronic structure calculation of $LiPbI_3$ has been carried out. The optimized parameters are kinetic energy cut off (ecutwfc) = 40 Rydberg, k-point = 5x5x5 grid and lattice constant = 6.3725 Å. Using these optimized parameters, the electronic structure of $LiPbI_3$ has been obtained with a direct band gap of 1.45 eV. The present results show that $LiPbI_3$ properties are different from $CsPbI_3$, but it may have a semiconductor property that can be also used as a photovoltaic material.

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