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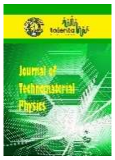

An In-depth Study of Relation Between Band Gap Energy and Lattice Constant for Cubic Phase $LiSnX_3$ (X = F, Cl, Br, and I) Perosvkite

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ABSTRACT

Organic perovskites or inorganic perovskites are very popular among researchers who are designing the most efficient perovskite solar cells. Besides, they can be used as materials for other optoelectronic applications, such as light-emitting diodes. In this paper, we reported the results of studies on the electronic property of $LiSnX_3$ (X = F, Cl, Br, or I) perovskite in the cubic phase. This electronic property is the density of states, which one can determine the band gap energy value. These studies were undertaken to understand the relation between their band gap energy and lattice constant through anion X variations. The Quantum ESPRESSO program calculated These two crucial quantities with norm-conserving Troullier-Martins pseudopotentials and Generalized Gradient Approximation Perdew-Burke-Enzerhof exchange-correlation functional. The computation results show that the band gap energy ranged from 0,3 eV to 0,99 eV while the lattice constant ranged from 6,183 Å to 4,625 Å for anion halide from I till F, respectively. The contrast trend between these quantities' values matches the Kronig-Penney Model.

Keywords: Kronig-Penney Model, Quantum ESPRESSO, perovskite LiSnX3, Band Gap Energy, Lattice Constant

ABSTRAK

Organik perovskit dan anorganik perovskit sangat populer di kalangan peneliti untuk mendesain sel surya perovskit yang paling efisien. Selain itu, mereka dapat digunakan sebagai bahan untuk aplikasi optoelektronik lain seperti dioda pemancar cahaya. Pada jurnal ini, kami melaporkan hasil penelitian tentang sifat elektronik perovskit $LiSnX_3$ (X = F, Cl, Br, atau I) dalam fase kubik. Properti elektronik ini adalah kerapatan keadaan yang dapat menentukan nilai energi celah pita. Penelitian ini dilakukan untuk memahami hubungan antara energi celah pita dan konstanta kisi melalui variasi anion X. Kedua besaran penting ini dikalkulasi dengan program Quantum ESPRESSO dengan pseudopotensial *norm-conserving* Troullier-Martins dan fungsi korelasi pertukaran Perdew-Burke-Enzerhof yang digeneralisasi. Hasil perhitungan menunjukkan bahwa energi celah pita berkisar antara 0,3 eV ke 0,99 eV sedangkan konstanta kisi berkisar antara 6,183 Å ke 4,625 Å untuk anion halida dari I sampai F. Kami menemukan bahwa tren kontras antara kedua ini ternyata cocok dengan Model Kronig-Penney.

Kata kunci: Model Kronig-Penney, Quantum ESPRESSO, Perovskit $LiSnX_3$, Energi Celah Pita, Konstanta Kisi

1. Introduction

Solar energy is energy in the form of light and heat from the sun. It can be utilized using various technologies, such as solar heating, solar photovoltaics, solar thermal electricity, solar architecture, and artificial photosynthesis. Of the several alternative renewable energy sources, solar energy is one of the most potential energy sources to be developed. The development of solar cell technology itself has undergone very significant development, marked by the emergence of new generations of solar cells from conventional silicon-based solar cells, then thin film solar cells to Dye-Sensitized Solar Cell (DSSC), which is the third generation of solar cells [1]. Compared to other solar cells, silicon-based solar cells such as multijunction silicon solar cells and single crystal solar cells have high efficiencies of 46% and 25%, respectively. However, these solar cells require difficult fabrication and are costly. Therefore, the development of solar cells with easy fabrication at low cost is still a hot topic in research. Perovskite-type solar cells have recently attracted attention due to their significant development, as they have achieved more than 20.1% efficiencies in the past eight years [2].

Nowadays, perovskite materials that are widely used now are metal halide perovskite types. It has the general formula AMX_3 where A is a group I inorganic or organic cation, M is a metal cation Pb or Sn, and X is an anion of the halide group. The Metal halide perovskite, first reported as a high-efficiency solar cell material, has a type of metal halide organic perovskite, namely $MAPbI_3$ with A, which is an organic compound in the form of methylammonium (MA). After the report, there were many attempts to replace the organic compound methylammonium to obtain better stability, as it is very susceptible to moisture and oxygen [3]. Some researchers even tried to develop metal halide perovskites without organic compounds by replacing the organic cation A with inorganic cations from group IA [4].

Many researchers have studied the substitution of cation or anion halide. Pitriana et al. have studied computationally the effect of substitution of various inorganic cations of group IA. They reported the results on the calculation of the band structure, density of states (DOS), lattice constant, projected density of states (PDOS), charge density, and bader charge analysis of $APbBr_3$ (where A is Li, Na, K, Rb, or Cs) by using Density Functional Theory (DFT) method [5]. Rahmani et al. used DFT method to calculate phonon properties, i.e., phonon dispersion and phonon density of states (PHDOS) of inorganic perovskite $CsSnX_3$ (X = Cl, Br, or I) in the cubic phase. They found that this perovskite was counted as an unstable molecule, although it still has an opportunity to be a solar cell active material [6]. Recently, Sidik et al. studied the optical properties of perovskite ABX_3 (A = Cs, Li; B = Pb; I = I, Br, or Cl) in the cubic phase using DFT. They concluded that this perovskite is a potential material for optoelectronic applications [7]. We predict that many research studies about determining phonon, electronic, optical, and even thermoelectric properties will come up in the future. Not only do they change the anion/cation, but they also change the other program to calculate them. However, one can see that those papers did not explain anything about why the lattice constant/band gap energy decreases/increases when those anions are exchanged.

This paper only focuses on determining the lattice constant and band gap energy value. The band structure will not be shown since one can obtain band gap energy from DOS. In other words, the primary purpose is to answer why the lattice constant/band gap energy value will decrease/increase when its anion halide is exchanged. Perovskite $LiSnX_3$ (X = F, Cl, Br, or I) in cubic phase was used because of its simplicity and scarcity in reports. As the researchers mentioned before, we also used the DFT method through the Quantum ESPRESSO (QE) program. The program works by implementing the Kohn-Sham equation, which cannot be solved analytically [8]. For this reason, we attempt to answer the decrease/increase trend by analogizing with a reasonable physical model.

2. Methods

The DOS value of $LiSnX_3$ (X = F, Cl, Br, and I) was computed with an open-source DFT computational program known as QE. Following this research's objective, we only focus on the crystal structures for these perovskites, which are the cubic Pm3m framework. They are visualized by the VESTA program, as shown in Figure 1. The inorganic cation (Li^+) is shown at the cubic corners, and the cubic center represents the divalent cation (Sn^{2+}), while every cubic face is filled with anion halogen (F^-, Cl^-, Br^-, and I^-) at the center. Besides, the norm-conserving Troullier-Martins pseudopotentials with Generalized Gradient Approximation Perdew-Burke-Enzerhof exchange-correlation functional (GGA-PBE) is used along the calculation. Each calculation is divided into two steps: optimizing input file parameters (cut-off energy, k-points, and lattice constant) and determining the DOS and their band gap energy.

2.1. Parameters Optimization

The most crucial component to be optimized in the beginning is cut-off energy. Its definition is the kinetic energy that limits the number of plane waves used in the calculation. They are divided into two types, i.e., cut-off energy for the wave function (ecutwfc) and cut-off energy kinetic energy for the charge density (ecutrho). In general, the ecutrho value is 8 times of ecutrho value. We varied the ecutwfc value in the range of 10–70 Rydberg. The second component to be optimized is k-points, which is attributed to the summation of a finite number of k-points to integrate k in the Brillouin Zone (BZ). This program uses Monkhrost-Pack variation k_1 x k_2 x k_3, where we varied from 1 x 1 x 1 to 7 x 7 x 7 (no shifting). Later, these k-points must be enlarged to 13 x 13 x 13 to get a denser grid in nscf calculation. The final optimization parameter to be determined is the lattice constant. It is performed through vc-relax calculation continuously until there is no change between the new and old lattice constant. After optimizing those three parameters, we perfomed the scf and nscf calculation. Finally, module dos.x was executed to obtain the DOS value. The DOS versus energy graph is plotted by gnuplot program. All of these processes will be applied to each perovskite. We did not discuss the partial density of states since this study only focuses on the band gap energy value. To ensure the reader understands our results, the same perovskite, either lattice constant or band gap energy from another journal, will be compared to our data.

2.2. *Crystal structure of $LiSnX_3$*

We chose the crystal structure of $LiSnX_3$ in a cubic phase where the Li atom lies at each cubic corner, the Sn atom lies at the cubic center, and the X atom lies at each cubic phase. For example, the cubic crystal of $LiSnI_3$ is shown in Figure 1.

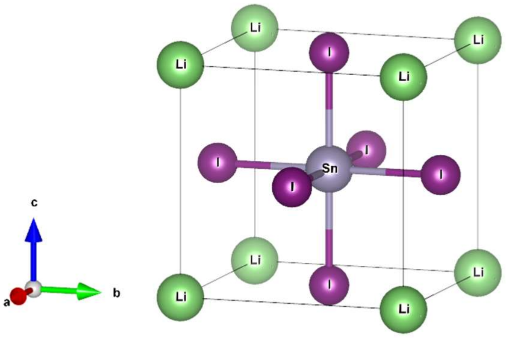

Figure 1. Crystal structure of perovskite $LiSnI_3$

3. Results and Discussion

3.1. *Lattice Constant Optimization*

Since we calculate four variations of perovskite, we are limited to showing only the optimization process for $LiSnI_3$. This result is shown in Table 1. Initially, the lattice constant was set to 5.0 Å because the $LiSnI_3$ optimum lattice constant from reference [9] is 6.158 Å. Table 1 shows the optimum lattice constant is 6.183 Å, obtained after the second iteration. The third iteration was executed to prove that the next iteration would produce the same result. One can see –76,825 Ry is the lowest among other results. The percentage deviation between our result and the reference is categorized as rational, i.e., 2.5 %. This slight difference appears because the pseudopotential and optimized k-point choices differ from ours, although the exchange-correlation functional type is identical.

Table 1. Lattice constant optimization of $LiSnI_3$

$a_{initial}$ (Å)	$a_{relaxation}$ (Å)	Total Energy (Ry)
5.000	6.089	-76.824
6.098	6.183	-76.825
6.183	6.183	-76.825

From Table 2, it can be directly seen that the lattice constants for all anions have a downward trend. The change in the atomic radius from the smallest (F) to the largest (I) causes a significant increase in the lattice constant of this $LiSnX_3$ perovskite.

Table 2. Optimized Lattice Constants of $LiSnX_3$

Anion X	$a_{relaxation}$ (Å)	Total Energy (Ry)
F	4.625	-152.561
Cl	5.529	-98.037
Br	5.806	-88.680
I	6.183	-76.825

3.2. The density of States of $LiSnX_3$

The total density of states (DOS) for $LiSnX_3$ (X = F, Cl, Br, or I) perovskite is shown in Figure 2. These DOS graphs provided information about how many electronic states at a certain energy per volume. If one looks closely, each curve of all perovskite seems to form a similar shape. Nevertheless, the value of the band gap (E_g) is the key to their differences. The band gap decreases in the following order of $LiSnF_3$, $LiSnCl_3$, $LiSnBr_3$, and $LiSnI_3$, i.e., 0.99 eV, 0.94 eV, 0.85 eV, and 0,3 eV, respectively. Compared with the reference [9], the percentage deviation for band gap energy $LiSnI_3$ falls into 1.3 %. This means that our results for $LiSnI_3$ and the others can be guaranteed. The difference may be due to the reason mentioned in part 3.1. Based on these four numerical band gap energy results, each perovskite's electronic property confirms that they are suitable as a component of perovskite solar cells.

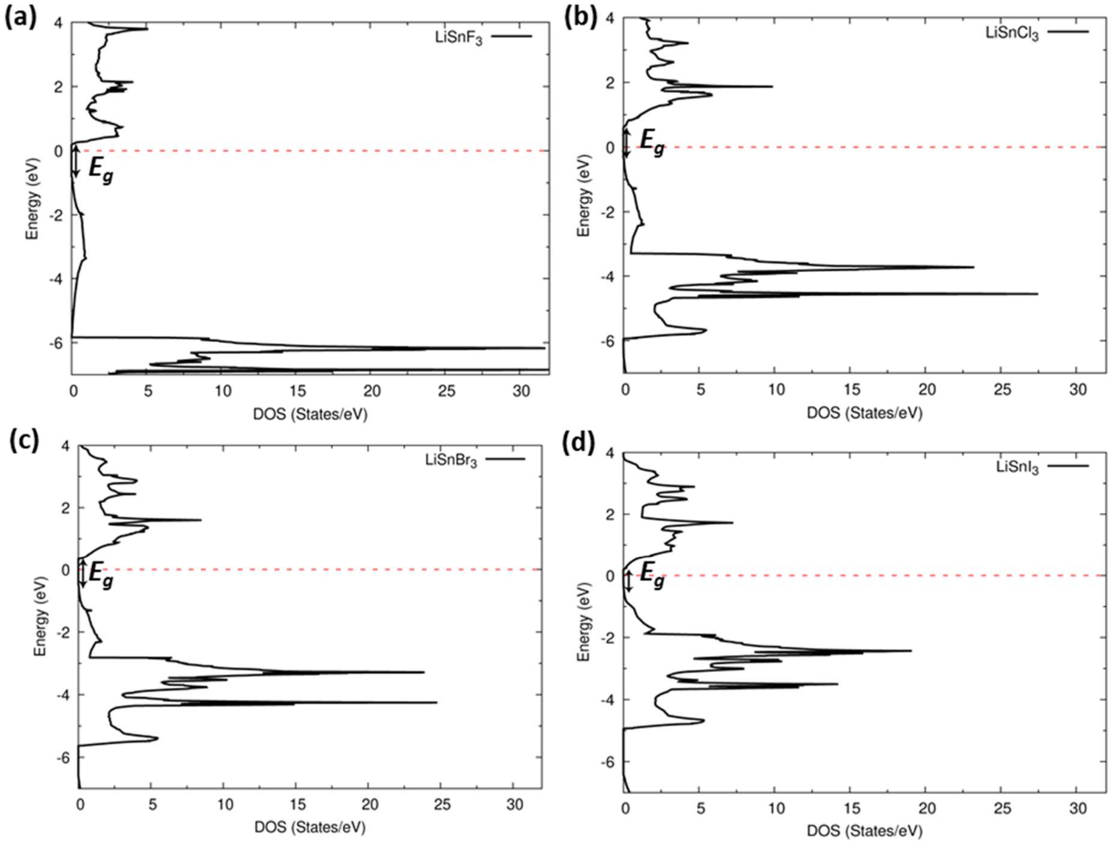

Figure 2. The density of states of (a) $LiSnF_3$, (b) $LiSnBr_3$, (c) $LiSnCl_3$, and (d) $LiSnI_3$ were calculated at their optimized lattice constants.

The trend between lattice constant and band gap energy is the opposite. Since no analytical solution is available to obtain DOS or band gap value, we try to connect this contrast trend to a reasonable physical model. The model that fits is the Kronig-Penney Model. This model discusses the behavior of electrons in a certain periodic potential, as shown in Figure 3.

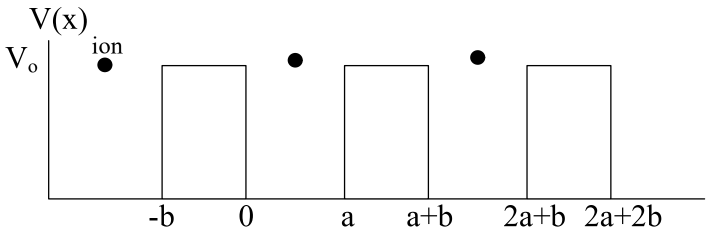

Figure 3. Periodic Rectangular Potential of Kronig-Penney Model [10].

For simplicity, the periodic potential was taken to be a delta Dirac function where V_o goes to ∞ , and b goes to 0, while V_ob still goes to finite. The eigenvalue equation yield (see reference [10] for more detail)

$$\left(\frac{P}{k_1a}\right)(k_1a)\ +cos\,cos\,(k_1a)\ =cos\,cos\,(ka)\,;\ P=\left(\frac{mV_0ba}{\hbar^2}\right) \qquad (1)$$

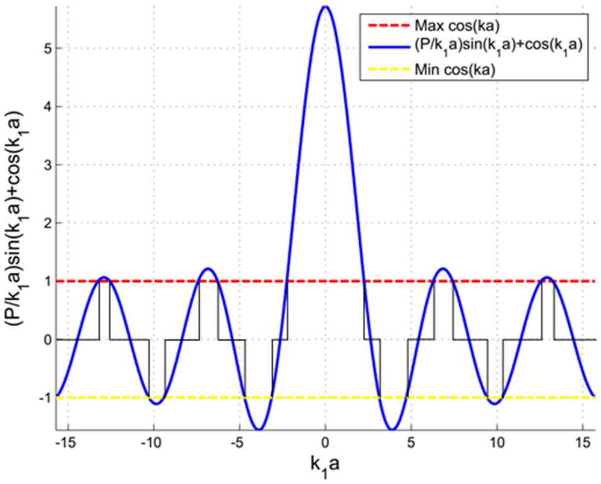

Figure 4. $\left(\frac{P}{k_1a}\right)(k_1a)\ +cos\,cos\,(k_1a)$ graph as the k_1a function for $P=3\pi/2$. The values of k_1a which produce $\left(\frac{P}{k_1a}\right)(k_1a)\ +cos\,cos\,(k_1a)$ in interval -1 dan +1 were shown by pieces (segments) of thin lines in k_1a axis [10].

From our previous research report, the plot of Equation (1) when $P=3\pi/2$ gives a simulation of Figure 4. Later, it concludes that the width of allowed band energy becomes wider, directly proportional to the increase of k_1a. The relation with our results is that the increase of k_1a can be analogous to the increase of the lattice constant. Assume one of those two thin black lines in Figure 3. is the conduction band while the other is the valence band. Next, we take an analogy to link this model to our results. We define a lattice constant ($a_{relaxation}$) of the researched perovskites as a constant. a can be assumed in this way because the distance between two rectangle potentials is related to the distance between two ions. By this analogy, one concludes that the longer the lattice constant of perovskite is, the smaller the band gap energy it has (e.g. $\propto$, $1/a_{\mathrm{relaxation}}$).

4. Conclusion

In this study, the density of states has been obtained for four variations of $LiSnX_3$ anion with optimization of lattice constants. From these densities of states, there is a varying energy gap value for each of the anions, ranging from 0.3 eV to 0.99 eV. On the other side, each anion has a varying lattice constant value ranging from 4.625 Å to 6.183 Å from I to F, respectively. The contrast trend between these two quantities fits the Kronig-Penney Model, where the lattice constants are the lengths between two periodic rectangular potentials.

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