Ab-initio calculation of APbI$_3$ (A=Li, Na, K, Rb and Cs) perovskite crystal and their lattice constants optimization using density functional theory

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Abstract. Halide perovskite materials APbI$_3$ (with A is inorganic alkaline cation) have received many attentions in some recent years related to the rapid progress of perovskite solar cells. Particularly, CsPbI$_3$ perovskite has been much investigated due to relatively more stable in comparison to other inorganic cation while its energy conversion efficiency has reached 10.5%. In this study, we report our calculation results of the geometric structure and the electronic structure of these inorganic perovskites with various alkaline cation. The calculations were performed by employing the Density Functional Theory (DFT) method using Quantum Espresso computational software package. The calculation employed variable-cell relaxation algorithm (vc-relax) to obtain the lowest total energy value and the corresponding Density of States (DOS). In addition, Ultrasoft pseudopotentials and PBE exchange-correlation functions were used. The cut-off of kinetic energy was set at 40 Rydberg and the k-point was set at 5x5x5. The computation results lead to the energy gap range in 1.40 eV to 1.46 eV. In addition, there is also an agreement between the electronic band structures and the DOS distribution pattern for optimum lattice constant.

1. Introduction
The fourth-generation solar cells based on perovskite-based crystal have attracted much attention due to high solar energy conversion efficiency. The highest efficiency (experiment) was reported at 22.1% by Nazeeruddin (2016) [1] while theoretically, as reported by Yin et al, it can reach 31.4% [2]. Recent reports by Beal et al. show that until 2016, perovskite-based crystal solar cell has achieved six times efficiency since its emergence in 2009 [3]. Both experimental and theoretical results were obtained from the perovskites consisting of organic cations and inorganic halides. One of the weaknesses of this kind of perovskites is its poor chemical stability. All-inorganic perovskite has been also extensively studied to solve the chemical instability problems in these perovskite solar cells. At least, this type of perovskite solar cells can achieve the conversion efficiency of 10.77% with stability for up to two months [4]. For understanding on the rule of the alkali cations on the perovskites characteristics and
the conversion efficiency of their solar cells, in the present study we investigated the role of alkali cation in the formation of electronic structures in all-inorganic perovskite, as well as how the role of each ion in forming the valence band and the conduction.

2. Computational Details
Before performing the electronic calculations of APbI$_3$ (A = Li, Na, K, Rb and Cs), the optimization of some calculation parameters were done firstly. From the five input file parameters mentioned by Giannozzi et al [5], in the previous calculation, it is known that the optimization of lattice constants is the most crucial and faster part to produce a convergent calculation. The optimization of lattice parameters is carried out by taking the initial lattice constants smaller than the reference, which is lit up until the condition is found that there is no significant change of the lattice constant and the total energy. The initial lattice constant of APbI$_3$ is 4.3 Angstrom. Calculation of pwscf (plane wave self-consistent field) module is done by relaxation of variable-cell which will minimize total energy by changing the position of the atoms in cell parameters used. The kinetic energy value of the cut-off wave function used is 40 Rydberg and the kinetic energy cut-off for the charge density is defined at 320 Rydberg. In the calculation of total energy, Brillouin zone of 5x5x5 was used and enlarged to 11x11x11 in order to get denser electron coverage. The pseudopotential type used is ultrasoft with the Rappe Rabe Kaxiras Joannopoulos method and the functional type of scalar relativistic exchange-correlation Perdew-Burke-Ernzerhof (PBE).

Figure 1. APbI$_3$ Perovskite (a) cubic crystal structure with an initial lattice constant 4.3 Å, and (b) electron path for the cubic system.

After the calculation of the total energy, the electronic structure of APbI$_3$ is calculated by using the module bands.x with large k-point. The electron path used for the cubic system is $\Gamma$-X-M-$\Gamma$-R-X-R [6]. The crystal structure and the electron path are shown in Figure 1. The density of states (DOS) and projected density of states (PDOS) can be calculated by using the dos.x and projwfc.x modules. The obtained DOS can display the total state density for all atoms, while the for PDOS will reflect each orbital of each atom.

3. Result and Discussion
3.1 Lattice Constants Optimization
The results on the optimization of lattice constants for APbI$_3$ for Rb cation are shown in Table 1. It seems that for this RbPbI$_3$, the initial lattice constant relaxed to 6.0765 Å. This value became the starting value for the second optimization calculation. This lattice constant value enlarged until the smallest total energy value was obtained, which was the condition for the optimization was completed. From Table 1, the total energy value did not enlarge further when the lattice constant of 6.366 Å was achieved. The optimization results for the other cations are shown in Table 2.
### Tabel 1. Lattice Constants Optimization of RbPbI₃

| $a_{\text{initial}}$ (Å) | $a_{\text{relaxation}}$ (Å) | Total Energy (eV) |
|--------------------------|-----------------------------|-------------------|
| 4.300                    | 6.0765                      | -5640.908         |
| 6.0765                   | 6.3661                      | -5641.167         |
| 6.3661                   | 6.3660                      | -5641.167         |
| 6.3660                   | 6.3656                      | -5641.167         |

From Table 2, it can be seen that the lattice constants for all cations have almost the same value of about 6.3 Å. The change in the atomic radius from the smallest (Li) to the largest (Cs) cause just a small increase in lattice constant of this APbI₃ perovskite.

### Tabel 2. Optimized Lattice Constant of APbI₃

| Cation | $a_{\text{relaxation}}$ (Å) | Total Energy (eV) |
|--------|-----------------------------|-------------------|
| Li     | 6.321                       | -5112.825         |
| Na     | 6.331                       | -6213.891         |
| K      | 6.352                       | -5693.103         |
| Rb     | 6.366                       | -5641.177         |
| Cs     | 6.376                       | -5540.861         |

#### 3.2. Band Structure and Density of States (DOS/PDOS) of APbI₃

The calculation of electronic band structure provides information on electron wave functions at wavenumber ($k$) and a certain energy. Figure 2 shows the electronic band structure for APbI₃ compounds with variations in the cations of Li, Na, K, Rb and Cs. From Figure 2, the left part shows the electronic band structure while the right part shows the density of states (DOS). All electronic structures have an almost identical shape on the valence band, while the structure of the conduction band is different. The valence band itself is a band filled with electrons. In Figure 2, the valence band is below Fermi ($E_F$) energy, while the conduction band is above $E_F$.

The empty area between the conduction band and the valence band shows the amount of energy that the electron must have in order to move from the valence band to the conduction band. The energy difference between the lowest energy of the conduction band (minimum band conduction/CBM) and the highest energy from the valence band (valence band maximum/VBM) is called the energy band gap ($E_g$) [7].

The CBM and VBM values from the electronic band structure that have been obtained for APbI₃, both are in the symmetry point R which is filled with cation A (Li, Na, K, Rb and Cs). The same k-point value from CBM and VBM shows that the energy band gap is a direct band gap. The value of the energy band gap of the five electronic structures of APbI₃ is shown in Figure 3.

The band gap energy was obtained from the APbI₃ calculation shows that the value is around 1.4 eV, with a little addition from Li to Cs. The addition of atomic radius from Li to Cs shows the addition of the energy band gap value from Li to Cs. Compared to the results obtained by Filip et al [8], the energy gap is influenced by the cation changes and the value decreases as the cation radius increases. Other computational results by Qian et al showed the value of the energy band gap for CsPbI₃ was 1.56 eV [9].

When compared with the results of experiments conducted by Dimesso et al. [10] showing a large difference of band gap energy for CsPbI₃ which is about 1 eV compared to the results of this calculation, this can occur considering that in measuring band gap energy experimentally carried out at room temperature, where the structure the crystal has changed, so that it is possible to change the value of the energy band gap.
Figure 2. The electronic structures and density of states (DOS) of APbI$_3$ calculated at their optimized lattice constants.

The PDOS curve of RbPbI$_3$ consists of 5s atomic orbital I (written I-5s), I-5p, Pb-5d, Pb-6s, Pb-6p, Rb-4s, Rb-4p and Rb-5s. Of all these orbitals, the dominant valence bands are filled with I-5p and Pb-6p. While the dominant conduction band is filled with Rb-5s and Pb-6p. The PDOS curves for four variations are not shown here. For five variations of the APbI$_3$ almost have the same pattern of atomic orbitals in the valence band and its conduction band. Anions are in the valence band, while cations are in the conduction band. The difference of the five compounds can be seen in the conduction band where the magnitude of PDOS for Li to Cs was decreased. This shows that electrons transferred to the anion in the valence band were increased from Li to Cs. The transfer of electrons is important as one of the good properties for light absorber material.

Figure 3. (a) PDOS from RbPbPI$_3$ and (b) band gap energy of APbI$_3$

From the electronic structure calculation results for this APbI$_3$, it seems that the perovskite crystals have band gap energy as a semiconductor material. Cation changes in crystals tuning the value of band gap energy. If referring to the Shockley Queisser boundary which states that 35% energy conversion efficiency can be achieved by a p-n connection solar cell device with a large energy band gap of 1.34 eV [11], the APbI$_3$ perovskite is likely to become a light absorber material with a large energy conversion efficiency.

4. Conclusion
In this study, electronic structures have been produced for five variations of APbI$_3$ cation with optimization of lattice constants. From these electronic structures, there is a varying energy gap value for each of the cations ranging from 1.40 eV to 1.46 eV and corresponding to the potential gap energy range for use as a light absorber material. From the DOS data, can be confirmed in the conduction
band filled with alkali cation and Pb, while in valence band consist of anion I dominantly. The APbI$_3$ perovskite could be potential light absorber material due to bandgap limit of Shockley Queisser boundary.

Acknowledgment
The authors would like to acknowledge the support from P3MI ITB program.

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