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Electronic Structure Calculations of Alkali Lead Iodide APbI_3 ($\text{A}=\text{Li}, \text{Na}, \text{K}, \text{Rb}$ or Cs) using Density Functional Theory (DFT) Method

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Abstract. The electronic structures of alkali lead iodide APbI_3 (where $\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$ or Cs), as one type of all-inorganic perovskites, have been investigated by the first-principles calculations based on Density Functional Theory (DFT) using Quantum Espresso package. The calculation results show that their electronic structures are slightly affected by the alkali atom A , leading to a slight variation in band gap and density of states (DOS) distribution. Prior to electronic structure calculations, the cell structures were optimized through the scheme of VC-relax calculation, including the optimization of kinetic energy cut-off and k-point. Their energy gaps were found to be in the range of 1.31 eV - 1.43 eV, despite their lattice parameters were significantly different ranging from 5.1 Å up to 6.3 Å. In general, these calculation results show that these alkali lead iodide perovskites are semiconductor materials and applicable as a sunlight absorber in solar cells, as reported elsewhere.

1. Introduction

Recently, organic lead halide perovskite materials have attracted much attention for solar cell applications. There are many reports showing that solar cells using this kind of perovskite produced high power conversion efficiency (PCE) larger than 15% in lab-scale devices. Accordingly, there are also many studies on their electronic structure calculations for explaining the origin of these perovskite characteristics. While the role of organic groups in these perovskite crystals is still further investigated, it is also interesting to investigate the possibility of the all-inorganic lead halide perovskites APbX_3 , such as CsPbX_3 , as an active material in solar cells [1]. There have been reported that solar cells using caesium lead iodide (CsPbI_3) produced PCE ranging from 5.95% up to 10.5% [1-3]. Although the efficiency is lower in comparison to the organic lead halide perovskite-based solar cells using, these all-inorganic lead halide perovskites are considered to be more practical due to less sensitive to humidity in their preparation process. In addition, these perovskites are more easily to be calculated because of the simplicity in their crystal structure and crystal symmetry. The calculation works on their electronic structures may be useful for understanding the role of the alkali metal A to the formation of their electronic structures and electronic properties. In this work, we investigated the electronic structures of



alkali lead iodide APbI₃ (where A=Li, Na, K, Rb or Cs) by performing the first-principles calculations based on Density Functional Theory method with the Quantum Espresso software package.

2. Computational Details

The calculations of the electronic structures of APbI₃ were carried out by Density Functional Theory (DFT) method with the Quantum Espresso software package [4]. Prior to the electronic structure calculation, the crystal structures of those perovskites were firstly optimized by performing the VC-relax calculations using Rabe Rappe Kaxiras Joannopoulos (Ultrasoft Pseudopotentials) and Perdew-Burke-Ernzerhof (PBE) of scalar relativistic exchange-correlation functional. These calculations optimized some parameters such as total energy, kinetic energy cut-off, lattice parameter and k-point. In order to truncate the plane wave expansion, the kinetic energy cut-off values of the wavefunctions were limited to 40 Ry.

The periodic system of APbI₃ was defined as the Pm3m cubic framework, which is correlated to the cubic structure of CsPbI₃. The lattice constant was taken from experimental results [1] for CsPbI₃, while it was set by considering their atomic radii for another compound. A typical crystal structure for the input of the calculation is shown in Figure 1. The Brillouin zone was determined by adopting the Monkhorst-Pack with 5×5×5 mesh for all of these APbI₃ crystals. Due to the presence of Pb atom, the SCF convergence problems may cause the band-crossings above or below the Fermi level. This problem was overcome by using the Methfessel-Paxton smearing type with 0.01 smearing width [5].

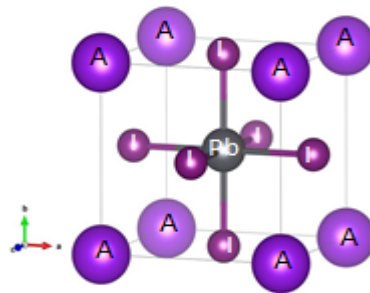


Figure 1. The typical crystal structure of APbI₃, where A=Li, Na, K, Rb and Cs with the lattice parameters $a = 5.1 \text{ \AA}$, $5.2 \text{ \AA}$, $5.6 \text{ \AA}$, $6.3 \text{ \AA}$ and $6.3 \text{ \AA}$, respectively

3. Result and Discussion

3.1. Electronic Band Structure of APbI₃

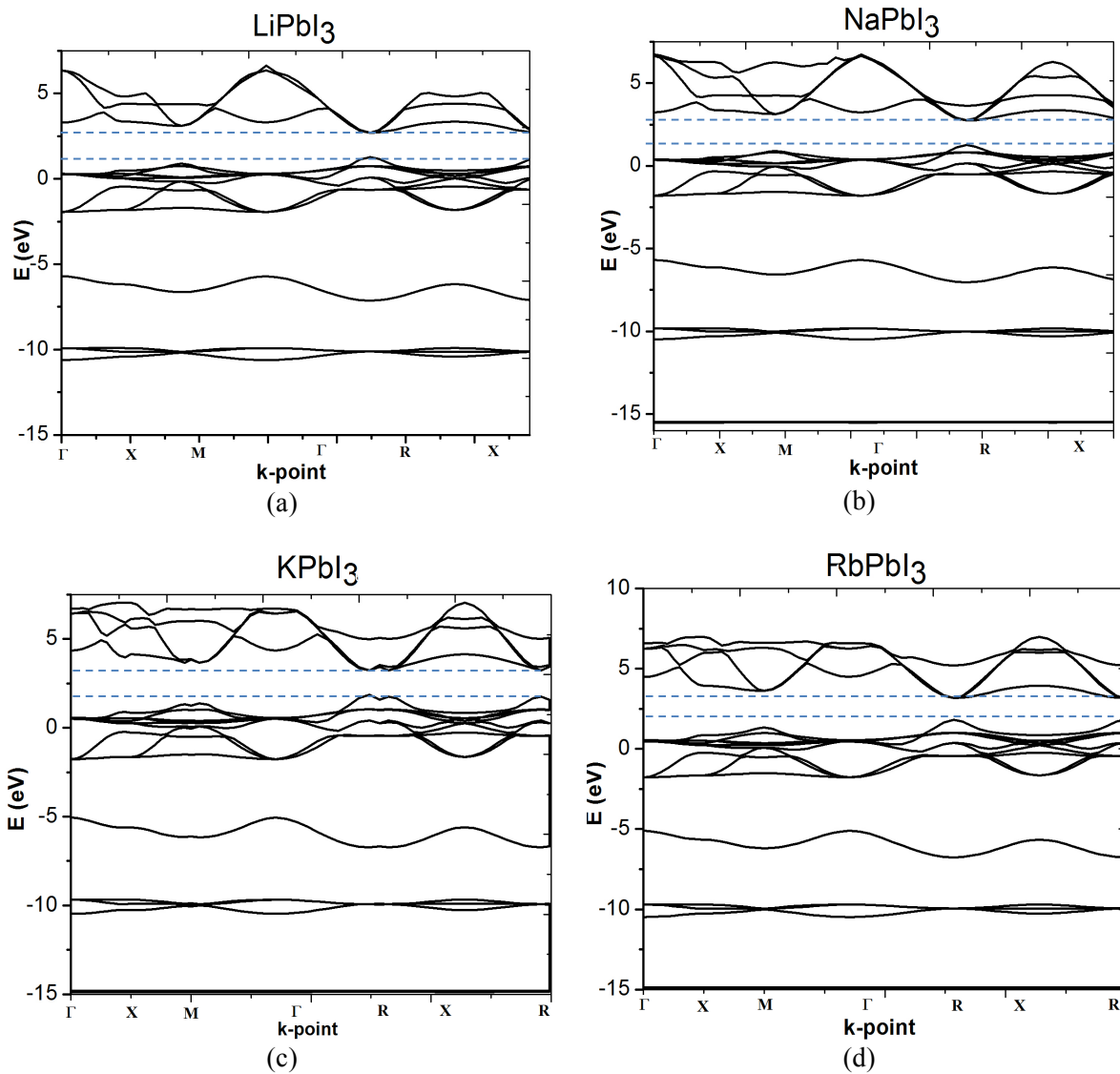
The calculation results of electronic structures for LiPbI₃, NaPbI₃, KPbI₃, RbPbI₃ and CsPbI₃ are shown in Figure 2. The k -axis is taken for a path along Γ -X-M- Γ -R-X-R of the cubic structure [6]. The band gap energy for each crystal was determined from these electronic structures, which is indicated by the gap in the electronic structure that present in the Fermi energy level. The band gap energy was then assigned as the gap between the highest value at valence band and the lowest energy at conduction band, which is indicated as the area in between two horizontal dashed-lines in Figure 2. These band gap energies were summarized in Table 1. In term of photon wavelength, all of these crystals have broad absorption band extending up to the near-infrared region, which may effectively absorb the sunlight spectrum and suitable as sunlight absorber in solar cells.

The band gap energies for these five crystal systems seem to be strongly correlated with the alkali cation element. The band gap decreases in the following order of NaPbI₃, LiPbI₃, RbPbI₃, KPbI₃ and CsPbI₃. In comparison to the experimental result by Dimesso *et al.* [7], the band gap energy of each system (except RbPbI₃) is relatively still much smaller. They reported that the band gap energies for LiPbI₃, NaPbI₃, KPbI₃ and CsPbI₃ were 2.30 eV, 2.36 eV, 2.19 eV and 2.40 eV respectively. The difference may be due to the difference in the crystal structure, where a cubic crystal structure was adopted in this present calculation work. The APbI₃ perovskites resulted from the experimental works

possess an orthorhombic crystal structure as they are formed at room temperature. However, a comparison with the calculation results by Filip *et al.* [8], the present results seems close to their results where the gap energies for LiPbI₃, NaPbI₃, KPbI₃ and CsPbI₃ are 1.79 eV, 1.72 eV, 1.70 eV, 1.65 eV and 1.53 eV, respectively.

Table 1. The band gap energies of LiPbI₃, NaPbI₃, KPbI₃, RbPbI₃ and CsPbI₃ obtained in this work.

	E_g (eV)	λ (nm)
LiPbI₃	1.43	867.13
NaPbI₃	1.48	837.84
KPbI₃	1.36	911.76
RbPbI₃	1.37	905.11
CsPbI₃	1.31	946.56



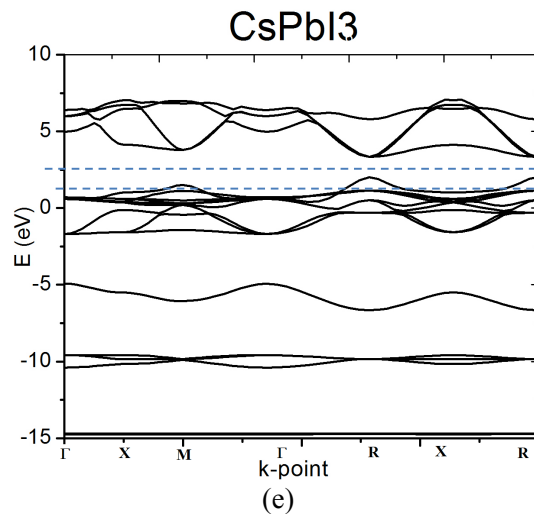


Figure 2. The electronic band structures of (a) LiPbI_3 , (b) NaPbI_3 (c) KPbI_3 (d) RbPbI_3 and (e) CsPbI_3

The total Density of State (DOS) and the corresponding PDOS (Projected Density of State) spectra for the selected APbI_3 crystals, namely RbPbI_3 and CsPbI_3 , are shown in Figure 3. The DOS gives the density or number of allowed electron states at given energy per volume. Figure 3 shows the consistency between the DOS spectra and the band structure. PDOS provides the projection of DOS values at each atomic orbitals. From these spectra, it is clear that their valence bands are constructed by the s -orbitals of Γ while their conduction bands are constructed by the p -orbitals of Pb^{2+} .

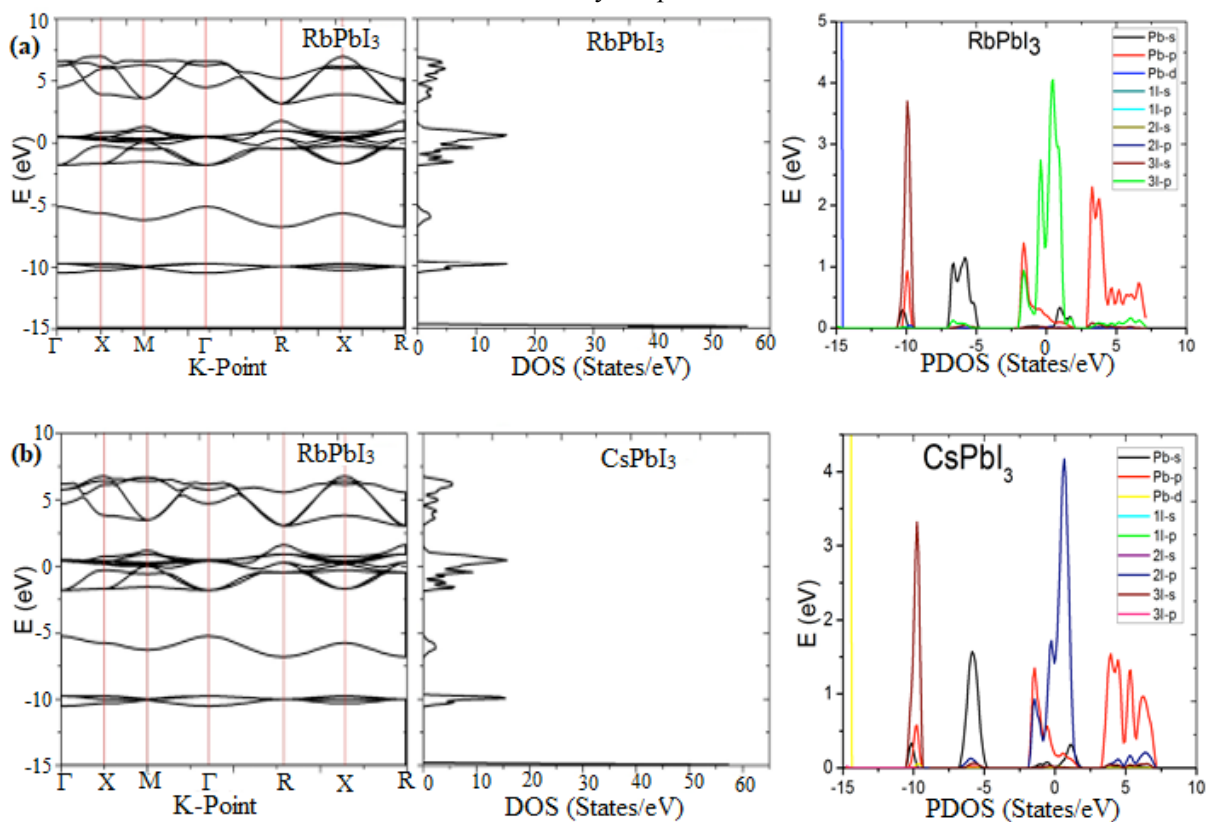


Figure 3. DOS and PDOS of (a) RbPbI_3 and (b) CsPbI_3

4. Conclusion

The electronic structures of cubic APbI₃ crystals have been calculated by employing the DFT method. The calculation results show that these perovskites have semiconductor properties with a small energy gap and a direct bandgap structure, which are slightly influenced by the alkali metal element A in the crystal. The energy gaps obtained in the present calculation work are slightly different from other reports, which may be due to the difference in the pseudofunction type and the use of cubic crystal structure in the present calculation work.

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