Electronic Properties of a New All-Inorganic Perovskite TlPbI₃ Simulated by the First Principles

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Abstract

All-inorganic perovskites have been recognized as promising photovoltaic materials. We simulated the perovskite material of TlPbI₃ using ab initio electronic structure calculations. The band gap of 1.33 eV is extremely close to the theoretical optimum value. Compared TlPbI₃ with CsPbI₃, the total energy (−3980 eV) of the former is much lower than the latter. The partial density of states (PDOS) of TlPbI₃ shows that a strong bond exists between Tl and I, resulting in the lower total energy and more stable existence than CsPbI₃.

Keywords: All-inorganic perovskite, TlPbI₃, CsPbI₃, First principles

Background

Hybrid organic–inorganic halide perovskites ABX₃ (A is an organic cation, B is Pb or Sn, and X is a halide) have been widely used as solar cells and attracted enormous interest due to the low-cost and simple solution process for extensive production in the field of photovoltaic (PV) applications. The rapid rise of hybrid organic–inorganic perovskite solar cells has seen photoelectric conversion efficiencies rise from 3.8% [1] to 21.1% [2] in less than 6 years, although the fact that the perovskite absorber layers are subject to degradation because of heat and humidity. To overcome these issues, numerous investigations on enhancing the efficiency [3, 4] and long-term stability [5, 6] have been performed for years [7–12], and now, the perovskite with all-inorganic structure is a primary focus [13]. For solar cells, an appropriate band gap will give a satisfactory efficiency. And the band gap should be narrow enough to absorb a broad solar spectrum from near infrared to visible light. The open-circuit voltage Voc is always lower than the band gap energy because thermodynamic detailed balance requires the cell to be in equilibrium with its environment, which indicates that there is spontaneous light emission from the cell. Considering the two factors, the cubic cesium lead iodide (CsPbI₃) is a promising candidate for PV devices. Reference [14] reported the maximum efficiency occurs for a semiconductor with a band gap of 1.34 eV and is 33.7%.

The outer electron configuration of the thallium atom is [Xe]⁴⁷¹⁴⁵d⁶⁶s²⁶p¹, which has two valence states of +1 and +3, +1 valence compounds are more stable than +3 [15]. In this paper, we simulated the perovskite material of TlPbI₃ with a band gap of 1.33 eV using ab initio electronic structure calculations based on the Density Functional Theory (DFT), and the band gap is extremely closer to the theoretical optimum value than CsPbI₃ (Figs. 1 and 2). Compared TlPbI₃ with CsPbI₃, the total energy (−3980 eV) of the former is much lower than the latter. The partial density of states (PDOS) of TlPbI₃ shows that a strong bond exists between Tl and I, resulting in the lower total energy and more stable existence than CsPbI₃. Besides, we calculated the carrier concentration and found both the two materials indicate similar carrier concentration ranged from −20 to 50 °C.

Methods

We employed ab initio electronic structure calculations with DFT and the generalized gradient approximation.
(GGA) [16] put forward by Perdew–Burke–Ernzerhof (PBE) [17]. We used plane-wave basis sets and pseudo-potentials. Kohn and Hohenberg [18] suggested that the real density of electrons would lead to a quite tiny functional value. Thus, Shan and Kohn optimized and put forward the density functional theory again, namely Kohn–Sham equations (KS equation) [19]:

$$\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}) + v_{\text{H}}(\vec{r}) + v_{\text{xc}}(\vec{r}) \right] \phi_i = \varepsilon_i \phi_i$$

(1)

Formula (1) represents the motion of the electrons in the molecular system. Where, $v_{\text{ext}}(\vec{r}) = -\sum_{a=1}^{N} \frac{Z_a}{|\vec{r} - \vec{r}_a|}$ is the interaction between electrons and atoms, namely external potential. $v_{\text{H}}(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$ stands for the interaction potential between electrons. $v_{\text{xc}}(\vec{r})$ is the functional differential of exchange-correlation energy. $E_{\text{xc}}$, $v_{\text{xc}}(\vec{r}) = \delta E_{\text{xc}} / \delta \rho(\vec{r})$ represents the exchange-correlation potential. The effective potential $v_{\text{eff}} = v_{\text{ext}} + v_{\text{H}} + v_{\text{xc}}$ is mainly determined by electron density, which can be obtained by KS equation. Obviously, the equation can be solved by self-consistent field equations (SCF) if we know the exchange-correlation energy $E_{\text{xc}}$. After obtaining the self-consistent convergence charge density $\rho_0$, the ground-state energy of the system can be expressed as [20]:

$$E_0 = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \int \int \frac{\rho_0(\vec{r}') \rho_0(\vec{r}'')}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r}'' - \int v_{\text{xc}}(\vec{r}) \rho_0(\vec{r}) d\vec{r} + E_{\text{xc}}[\rho_0(\vec{r})]$$

$$\varepsilon_i$$ is the eigenvalue of Eq (1):

$$\varepsilon_i = \left< \frac{1}{2} \nabla^2 + v_{\text{eff}} \right> \phi_i$$

(3)

In theory, the KS equation derived from DFT should be accurate [21]. But in the specific case, as $E_{\text{xc}}$ is a function associated with the single electron density $\rho(\vec{r})$, it is necessary to find a function that can replace the single electron density. We can solve a set of $\phi_i$ by taking $v_{\text{xc}}$ into the KS equation. Then a new $v_{\text{xc}}$ can be calculated with this $\phi_i$. Finally, we submit it into KS equation and solve. Repeat the iteration until a certain accuracy. The key problem is to find the appropriate exchange correlation energy $E_{\text{xc}}$. In the case of different calculation methods of exchange correlation energy $E_{\text{xc}}$, a series of DFT models have been reported [22]. The GGA method is more accurate because it has been combined with
inhomogeneous electron gas to obtain $E_{\text{kin}}$, $E_{\text{el}}$, and other parameters [23].

To calculate out carrier concentration, we must know the effective mass of electron, expressed by the following formula [18].

$$m^*_e = \frac{\hbar^2}{d^2E/dk^2}$$  \hspace{1cm} (4)

As expressed in formula (4), effective mass of holes and electrons can be obtained by calculating the two derivatives of valence-band maximum and conduction-band bottom. Finally, the carrier concentration is obtained as follows:

$$n_i = \left(2.510 \times 10^{19}\right) \left(\frac{m^*_e}{m_0} \cdot \frac{m^*_p}{m_0}\right)^{\frac{3}{2}} \left(\frac{T}{300}\right)^{\frac{3}{2}} e^{-\frac{E_g}{kT}}$$  \hspace{1cm} (5)

$m^*_e/m_0$ is the effective mass of electron, obtained by:

$$\frac{m^*_e}{m_0} = \frac{\left(6.626 \times 10^{-34}\right)^2}{\alpha \times 1.6 \times 10^{-19} \times 9.109 \times 10^{-31}}$$  \hspace{1cm} (6)

of which, $\alpha$ is the two derivatives of conduction-band bottom. $a$ is the lattice constant. Instead of conduction-band bottom by valence-band maximum, the formula (6) is often applied to solve the effective mass of hole $m^*_p/m_0$ [24].

The Brillouin zone was sampled with a $2 \times 2 \times 2$ k-point set and built by $2 \times 2 \times 2$ supercell. The simulated models using $6s^24f^{14}5d^{10}$ and $5s^24d^{10}5p^6$ as valence electrons for Tl and Cs, respectively, are carried out. Firstly, we use the ultrasoft pseudopotentials to optimize the Pm3m structures of both TlPbI$_3$ and CsPbI$_3$. Then, we calculate the equilibrium volume and proper values of the lattice constants. After optimizing the crystalline structure, we calculate the total energy, band structure, density of states, and carrier concentration for two kinds of materials in the last.

### Table 1

|          | $X$ = Tl | $X$ = Cs |
|----------|----------|----------|
| X-Pb     | 5423 Å   | 5475 Å   |
| X-I      | 4428 Å   | 4471 Å   |
| Pb-I     | 3131 Å   | 3161 Å   |
| X-Pb-I   | 54.736 Å | 54.736 Å |

### Results and Discussion

Optimizing the geometry of TlPbI$_3$ and CsPbI$_3$, we have simulated that the lattice constants are 6.2621 Å and 6.3225 Å, respectively. The bond distances and bond angles calculated are presented in Table 1.

The total energies of TlPbI$_3$ and CsPbI$_3$ are $-3979.94 - 3154.36$ eV independently. The lower total energy means the better stability. Thus, a conclusion that TlPbI$_3$ has better stability than CsPbI$_3$ is summarized theoretically.

The band gap of both semiconductors are calculated out 1.763 and 1.331 eV, respectively. The absorption spectrum of CsPbI$_3$ measured by the experiment (Fig. 3a) shows the optical band gap is 1.73 eV, which is close to the simulated value. And the absorption decreases above the wavelength of ~716 nm. The outcomes further indicate that the model we simulated are correct. Both of their Fermi levels are extremely close to the valence-band maximum, meaning that they are p-type semiconductors.

The band gap of TlPbI$_3$ is quite close to the perfect semiconductor reported in reference [14]. If we can fabricate the solar cells with this material, a high efficiency will be obtained. However, the devices based on TlPbI$_3$ are limited to simulate because of the toxicity.

Here, we select the valence-band maximum and conduction-band minimum for further analysis. As shown in Fig. 3b, the curvature of energy band in TlPbI$_3$ is less than that in CsPbI$_3$. The conduction band of TlPbI$_3$ is relatively smooth and conducive to receive

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**Table 1** The bond distances and bond angels of TlPbI$_3$ and CsPbI$_3$

|          | X = Tl | X = Cs |
|----------|--------|--------|
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**Fig. 3**

*a* is the absorption spectrum of CsPbI$_3$ measured by experiment. *b* is the structures of valence-band maximum and conduction-band minimum of TlPbI$_3$ and CsPbI$_3$.
electron from valence band, enhancing the existence of carriers.

According to the molecular orbital theory [25], the corresponding to the bond or anti-bond orbitals are formed by the more gentle part of the band curve. As shown in Figs. 1 and 2, if the peak of DOS curve is quite sharp, the corresponding energy-band curve is smooth; if the peak of DOS curve is relatively flat, the energy-band curve is relatively curved. So it can be deduced that the molecular orbitals are consistent with the peaks of the DOS graph. The peak height in the PDOS diagram (shown in Fig. 4) reflects the number of electrons contributing to this peak. If the PDOS of two different atoms has the resonance peaks in the range of same energy, it means the two atoms have already bonded. However, it cannot be determined that whether the band or anti-band are formed by analyzing the PDOS without further experiments. When the existence of resonance peaks are caused by the interaction of several atoms, we cannot distinguish that the bonds are formed by the two specific atoms. The conclusion does not affect our analysis.

As illustrated in Fig. 4a–c, the conduction-band minimum of CsPbI₃ is mainly composed by 6p state of Pb, and the valence-band maximum is contributed by 5p states of I. In Fig. 4d–f, the bottom of the conduction band of TlPbI₃ is mainly composed by both 6p states of Tl and 6p states of Pb, and the top of the valence band is contributed by 5p states of I. As presented in Fig. 4d–f, Tl and I have a strong resonance peaks between −12 and −10 eV, resulting in a deep level state. It also explains why TlPbI₃ is more stable than CsPbI₃.

Finally, carrier concentration are calculated by formulas (5) and (6). The relationship between temperature and carrier concentrations of both TlPbI₃ and CsPbI₃ is shown in Fig. 5. The carrier concentration of TlPbI₃ is slightly less than that of CsPbI₃ because the electronegativity of Tl (2.04) atom is larger than that of Cs (0.79) atom [26]. A larger electronegativity leads to a larger ionic bond component and stronger polarity, enhancing the attraction between electrons.

Conclusions
We simulated the perovskite material of TlPbI₃ with a band gap of 1.33 eV using ab initio electronic structure
calculations and the band gap is extremely close to the theoretical optimum value. Compared TiPbI_3 with CsPbI_3, the total energy (~3980 eV) of the former is much lower than the latter. The partial density of states (PDOS) of TiPbI_3 shows that a strong bond exists between Tl and I, resulting in the lower total energy and more stable than CsPbI_3. Besides, we calculated the carrier concentration and found both the two materials have similar carrier concentration ranged from ~20 to 50 °C.

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Authors’ Contributions
ZL designed and carried out the simulations. ZL and TZ participated in the work to analyze the data and prepared the manuscript initially. YW, CW, PZ, HS, ZC, and SL gave equipment support. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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