



Electronic properties of CsPbI₃/TiO₂: A First-Principle Study

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Abstract

Due to suitable bandgap and high thermal stability, α -CsPbI₃ as a semiconductor in the cubic phase is an ideal candidate for optoelectronic applications including light-emitting diodes, lasers, light-to-electricity convertors, and quantum light emitters. In this work, using the density functional theory and first-principle calculations, we have characterized the structural stability and electronic properties of α -CsPbI₃ and TiO₂ (rutile) interfaces in (001) direction. We have investigated two different models comprising CsI/TiO₂ and PbI₂/TiO₂ interfaces. The results of the calculations show that the charge accumulation in the interface of PbI₂ and TiO₂ is larger than the CsI and TiO₂ in the (001) direction. This effect leads to the formation of a larger surface dipole on the two sides of the CsI/TiO₂ interface. In conclusion, as a result, the binding energy is decreased and so, the CsI/TiO₂ interface is less stable than the PbI₂/TiO₂ interface.

Keywords: perovskite, cesium lead iodide, titanium dioxide, interface, dipole correction.

Introduction

Recently, the possibility of using perovskite compounds in optoelectronic devices has received too much attention. Besides, due to their unique electronic and optical properties, perovskite structures are suitable candidates for use in semiconductor detectors[1].

Because of the relatively high diversity of perovskite structures, using computational design to determine the appropriate structures has a significant contribution in reducing the manufacturing costs and optimization of perovskite-based detectors. These structures are generally classified as organic-inorganic perovskites and inorganic perovskites. Halide perovskites containing organic molecules have excellent characteristics such as high efficiency, low cost and easy synthesis, and high carrier mobility, but show poor stability against high moisture and heat. All-inorganic perovskites have higher thermal stability and also, the charge-carrier mobility of them is similar to Halide perovskites containing organic molecules. Among them, α -CsPbI₃ (cesium lead iodide in cubic phase) because of the suitable bandgap of 1.73eV is an ideal candidate for optoelectronic applications[2-3].

In 2019, Wang et al. showed that rutile TiO₂ enhances the extraction and transportation of electrons and reduces the combination. This structure in comparison with anatase TiO₂ has better conductivity and an improved interface with the MAPbI₃ layer[4].

Accordingly, in this study, we considered two possible interface models of α -CsPbI₃ and TiO₂ (rutile) in (001) interface and the electronic properties and the stability of them established.

Methodology and computational details

All density functional theory (DFT) calculations were performed using the Quantum Espresso [5]. We employed the Perdew-Burke-Ernzerhof (PBE) approximation to the exchange-correlation functional along with norm-conserving pseudopotentials [6]. The

kinetic energy cutoff for the plane-wave basis set was set to 30 Ry and the first Brillouin-zone (BZ) integration was carried out using a $3 \times 3 \times 1$ Monkhorst-Pack mesh.

The approach introduced by Estrada et al., Which is implemented in QuantumATK software [7], has been used to simulate interfaces in (001) direction.

Results and discussion

The cubic crystal structure of α -CsPbI₃ has a space group of Pm-3m and TiO₂ has a tetragonal structure with a space group of P4₂/mm. In the first stage, the lattice constants of the bulk structures were optimized.

To simulate the interface, two possible termination CsI- and PbI₂ terminated slabs in (001) direction were employed for the next analysis. The interfaces are shown in Fig 1.

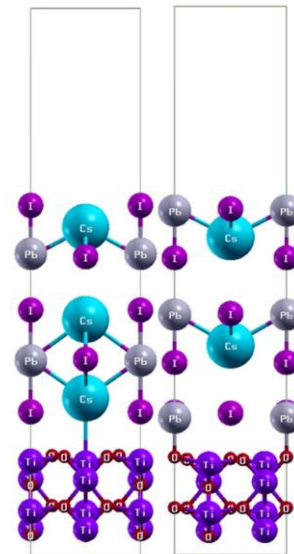


Figure 1: TiO₂-CsI (001) (left), TiO₂-PbI₂(001) (right).

To evaluate the stability of these structures, their binding energy (E_b) was calculated using Equation (1) [8] and the results are presented in Table 1.

$$E_b = E_{\text{TiO}_2\text{-CsI(PbI}_2)} - E_{\text{TiO}_2} - E_{\text{CsI(PbI}_2)} \quad (1)$$

Table 1: Lattice mismatch, layer space in the interface (d), binding energy (E_b), bandgap (E_g)

	Lattice mismatch	d(Å)	E_b (eV)	E_g (eV)
TiO ₂ -CsI	4.4%	3.04	-0.38	1.08
TiO ₂ -PbI ₂	4.4%	2.45	-0.71	1.46

Where $E_{\text{TiO}_2\text{-CsI(PbI}_2)}$ is the total energy of the interfaces, E_{TiO_2} is the total energy of TiO₂(001) surface and, $E_{\text{CsI(PbI}_2)}$ is the total energy of CsI(PbI₂)(001) surface. As shown in Fig 2, the charge accumulation in the interface of PbI₂ and TiO₂ is larger than the CsI and TiO₂ in (001) direction thus it is expected that stronger orbital bonds are formed and hence the binding energy must be larger for the PbI₂-TiO₂ interface.

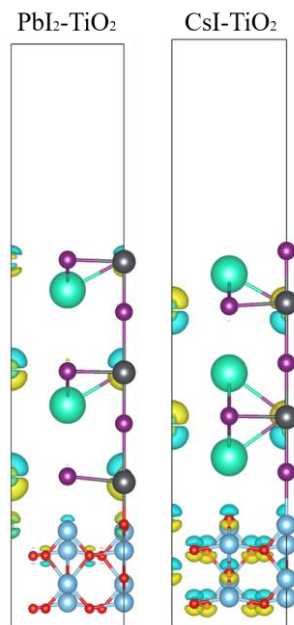


Figure 2: Average charge difference TiO₂-PbI₂ (right) and TiO₂-CsI (left).

The formation of asymmetric slabs leads to asymmetric polarization that leads to creating an artificial electric field in the slab. The usual method that is used to cancel the artificial electric field is the dipole correction[9]. We used this method to measure the surface dipole of the slabs. The laterally averaged electrostatic potential with and without dipole correction for two models interface is shown in Fig 3. For the PbI₂-TiO₂ slab, the amount of the dipole correction is 0.001a.u, whereas for the CsI-TiO₂ is 0.005a.u, which is five times the PbI₂-TiO₂ interface. Therefore, it is expected that the charge accumulation over the outer atomic layers of the CsI-TiO₂ slab is larger than the PbI₂-TiO₂ interface.

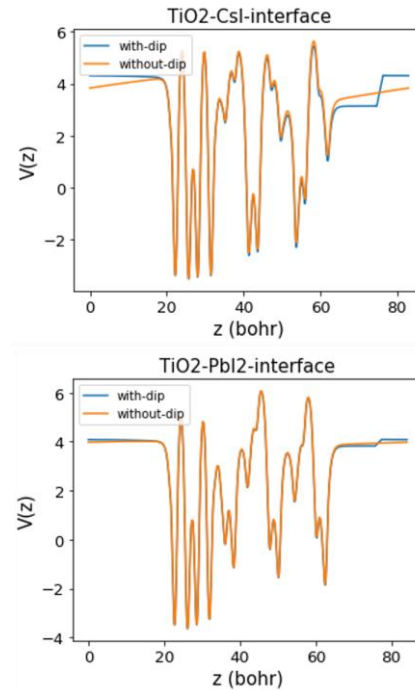


Figure 3: Electrostatic potential without (orange) and with (blue) for the TiO₂-CsI interface (above figure), for the TiO₂-PbI₂ interface (below figure).

Conclusions

In this study, we have calculated the binding energy of the two possible interfaces of α -CsPbI₃ and TiO₂ (rutile) in (001) direction. According to the results, the CsI-TiO₂(001) interface is less stable. This is due to the reduction of electron density in the interface, the more charge accumulation in the outer atomic layers, and therefore more unstable structure.

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