Defect Investigation of Ti-Based Vacancy-Ordered Double Perovskite Solar Cell using SCAPS-1D

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Abstract. Despite the great promise of lead-based perovskite solar cells, their inherent toxicity and stability issues have hindered their practical applications in solar cells. Titanium(Ti)-based vacancy-ordered double perovskite Cs₂TiBr₆ was proposed as a non-toxic and stable substitute for lead-based perovskites. However, the efficiencies of the Cs₂TiBr₆ double perovskite solar cells currently have a maximum value of only 3.28%, which is still far below typical perovskite solar cells. Since the bulk defects inside the Cs₂TiBr₆ absorber layer are the main reason for degrading the performance of the Cs₂TiBr₆ double perovskite solar cell, it is worthwhile to investigate the bulk defect density in the absorber layer to optimize the performance of the Cs₂TiBr₆ double perovskite solar cell. In this work, we simulate the Cs₂TiBr₆ double perovskite solar cell with the FTO/ SnO₂/ Cs₂TiBr₆/ PEDOT:PSS/ Au structure by using SCAPS-1D simulation software. We investigate the effect of the bulk defect density in the Cs₂TiBr₆ absorber layer for the performance of the Cs₂TiBr₆ double perovskite solar cell. The conclusion is that there is a threshold value for the bulk defect density in the Cs₂TiBr₆ double perovskite solar cell. Moreover, we obtain an optimal efficiency of 9.97% in the Cs₂TiBr₆ double perovskite solar cell by optimizing the bulk defect density. Our numerical simulation results show that the Cs₂TiBr₆ double perovskite solar cell has excellent potential and appropriate defect passivation is conducive for improving its performance.

1. Introduction
The performance metrics of lead-based organic-inorganic hybrid perovskites show the most promise among the emerging materials being studied to develop next-generation solar cells, leading to a rapid jump in the power conversion efficiency (PCE) of perovskite solar cells (PSCs), which now surpasses 25% [1]. Despite the great promise of lead-based PSCs, their inherent toxicity and stability issues due to the lead cation (Pb²⁺) and the volatile organic cations (MA⁺, FA⁺) have hindered their practical applications in photovoltaics (PV) [2-3]. To solve the two main obstacles mentioned above, the researchers proposed to replace lead cation (Pb²⁺) with tin cation (Sn²⁺) and germanium cation (Ge²⁺),...
which are in the same group IV as Pb, to obtain lead-free perovskite [4-5]. However, the efficiency of the device PSCs prepared by this method is usually less than 10%, which is much less than the efficiency of lead-based PSCs [4-5]. In addition, Sn and Ge are in the high-energy 5s and 4s orbitals, resulting in the easy oxidation of Sn\(^{2+}\) and Ge\(^{2+}\) to tetravalent cations, i.e., Sn\(^{4+}\) and Ge\(^{4+}\) [6]. Although this approach solves the toxicity problem of lead-based perovskites, these lead-free perovskites are not suitable for PV applications due to the low PCE and high instability of tin-based and germanium-based PSCs. Subsequently, researchers have proposed two-dimensional (2D) and zero-dimensional (0D) perovskites (e.g., Cs\(_3\)Sb\(_2\)X\(_9\) and Cs\(_3\)Bi\(_2\)X\(_9\) (X = Cl, Br, I)) to solve stability problem of lead-based perovskites [7-8]. However, the highest PCE in pure 2D planar PSCs is only 15.3%, which is lower than that of 3D PSCs [9]. Recently, double perovskite structure \(A_2B_1B_2X_6\) has been proposed as a promising candidate for achieving non-toxic stable and efficient PSCs by replacing two toxic lead ions with a pair of heterovalent (i.e., monovalent and trivalent) metal cations [10]. As the classic material of double perovskites, the Cs\(_2\)AgBiBr\(_6\) has a wide indirect bandgap of 2.19 eV, leading to a very low PCE of solar cell [11]. Recent reports have showed that the highest PCE of the PSCs based on Cs\(_2\)AgBiBr\(_6\) is only 2.5% [12]. Therefore, it is necessary to continue searching for suitable double perovskites for PSCs. Specifically, if one B-site ion is vacant and the other B-site ion is a tetravalent metal cation in the double perovskite structure, the resulting special double perovskite structure is also called vacancy-ordered double perovskite. These vacancy-ordered double perovskites (e.g., CsSnI\(_6\) and CsTeI\(_6\)) are considered by researchers to possess a direct bandgap, strong environmental stability, and strong light absorption.

In 2017, titanium(Ti)-based vacancy-ordered double perovskite Cs\(_2\)TiBr\(_6\) was proposed by Ju et al. with a direct bandgap of 1.78eV and strong environment stability under different conditions (humidity, heat, and light conditions) [13]. In 2018, Chen et al. prepared a Cs\(_2\)TiBr\(_6\) film with a direct bandgap of 1.8 eV for the first time by a two-step vapor deposition method and then fabricated a PSCs based on the Cs\(_2\)TiBr\(_6\) film with the structures of FTO/ TiO\(_2\)/ Cs\(_2\)TiBr\(_6\)/ P3HT/ Au and FTO/ TiO\(_2\)/ C\(_60\)/ Cs\(_2\)TiBr\(_6\)/ P3HT/ Au, which had the efficiencies of 2.26% and 3.28% [14]. In addition, the Cs\(_2\)TiBr\(_6\) PSC retained 94% of its initial performance after 14 days of storage in ambient air, which showed the high environment stability of the Cs\(_2\)TiBr\(_6\) PSCs. In 2019, Kong et al. prepared Cs\(_2\)TiBr\(_6\) thin films by solution synthesis for the first time, and this method reduced the cost of preparing the films, thus facilitating the preparation of Cs\(_2\)TiBr\(_6\) cells at a low cost [15]. Until now, to the best of our knowledge, the 3.28% efficiency of the Cs\(_2\)TiBr\(_6\) solar cell prepared by Chen is still the highest in the double perovskite solar cells (DPSCs). However, there is still very little understanding of the Cs\(_2\)TiBr\(_6\) DPSC, and it is significant to investigate the Cs\(_2\)TiBr\(_6\) DPSC further to improve its efficiency. Since the bulk defects inside the Cs\(_2\)TiBr\(_6\) absorber layer are the main reason for degrading the performance of the Cs\(_2\)TiBr\(_6\) DPSC, it is worthwhile to investigate the bulk defect density in the absorber layer to optimize the performance of the Cs\(_2\)TiBr\(_6\) DPSC.

In this work, we simulate the Cs\(_2\)TiBr\(_6\) DPSC based on the FTO/ SnO\(_2\)/ Cs\(_2\)TiBr\(_6\)/ PEDOT:PSS/ Au structure using simulation software. We investigate the effect of the bulk defect density in the Cs\(_2\)TiBr\(_6\) absorber layer for the performance of the Cs\(_2\)TiBr\(_6\) DPSC and then optimize the bulk defect density to obtain an optimal PCE.

2. Simulation Methods and DPSC Parameters

2.1. Simulation Methods

The numerical simulation software used in this study is SCAPS-1D, a 1D solar cell simulation software program developed by investigators at Ghent University. [16]. Fundamentally, SCAPS-1D executes three sets of PV equations for the hole and electron carrier densities, respectively [17]. These four equations are shown below:

\[
\frac{d}{dx} \left[ \varepsilon(x) \frac{d\psi}{dx} \right] = q[p(x) - n(x) + N_d(x) - N_a(x) + p_t(x) - n_t(x)] \tag{1}
\]
\[-\frac{1}{q} \frac{dJ_n}{dx} + R_n(x) - G(x) = 0 \quad (2)\]

\[-\frac{1}{q} \frac{dJ_p}{dx} + R_p(x) - G(x) = 0 \quad (3)\]

\[\alpha = A_\alpha (h\nu - E_g)^{\frac{1}{2}} \quad (4)\]

Where \(x\) is the coordinate position; \(\varepsilon\) is the relative permittivity; \(p\) denotes the number of holes; \(n\) denotes the number of electrons; \(p_t\) denotes the number of trapped holes; \(n_t\) denotes the number of trapped electrons; \(\psi\) represents the electrostatic potential; \(N_a\) represents the ionized acceptor concentration; \(N_d\) represents the ionized donor concentration; \(J_p\) denotes the current density of holes; \(J_n\) denotes the current density of electrons; \(R_p(x)\) is the recombination rate of holes; \(R_n(x)\) is the recombination rate of electrons; \(G(x)\) represents the optical generation rate; \(\alpha\) indicates the absorption coefficient of the material, and \(A_\alpha\) is 10^5.

2.2. DPSC Parameters

We simulate the DPSC with the FTO/ SnO\(_2\)/ Cs\(_2\)TiBr\(_6\)/ PEDOT:PSS/ Au structure. Figure 1 presents the schematic structure of the Cs\(_2\)TiBr\(_6\) DPSC. As the structure shows, we use PEDOT:PSS and SnO\(_2\) film as the hole transport layer (HTL) and the electron transport layer (ETL). FTO and Au are used as the negative and positive electrodes, respectively. Cs\(_2\)TiBr\(_6\) thin film is utilized as an absorber layer in the DPSC. The simulation parameters of PEDOT:PSS, SnO\(_2\), and Cs\(_2\)TiBr\(_6\) required for the simulation are presented in table 1 which extracted from the previously published literature [18-20]. For the interface defect of SnO\(_2\)/Cs\(_2\)TiBr\(_6\) and Cs\(_2\)TiBr\(_6\)/PEDOT:PSS, defect types are neutral, energetic distributions are Single, characteristic energies are 0.1 eV, energy levels with respect to the reference are 0.6 eV, total defect densities are 10\(^{-13}\)cm\(^{-3}\), electron capture cross-sections are 10\(^{-19}\)cm\(^2\) and 10\(^{-18}\)cm\(^2\), and hole capture cross-sections are 10\(^{-18}\)cm\(^2\) and 10\(^{-19}\)cm\(^2\). We set 1 \(\Omega\cdot\text{cm}^2\) and 4200 \(\Omega\cdot\text{cm}^2\) for the series resistance and the shunt resistance. As for the operating conditions of the DPSC, we use standard irradiation of AM1.5G and a continuous temperature of 300 K [18].

![Figure 1. Schematic structure of the Cs\(_2\)TiBr\(_6\) DPSC.](image)

| Parameter | Cs\(_2\)TiBr\(_6\) | PEDOT:PSS | SnO\(_2\) |
|-----------|-----------------|-----------|-----------|
| Thickness (nm) | 100 | 30 | 30 |
| \(E_g\) (eV) | 1.8 | 2.2 | 3.5 |
| \(\chi\) (eV) | 4 | 2.9 | 4 |
### 3. Results & Discussion

The recombination process of photo-generated hole-electron pairs in DPSCs occurs mainly inside the Cs$_2$TiBr$_6$ absorber layer, so it is vital to understand the effect of bulk defect density on the performance of the Cs$_2$TiBr$_6$ DPSC to achieve maximum PCE. To investigate the effect of absorber layer bulk defects on the DPSC performance, we calculated the cell parameters by varying the bulk defect density from $10^{11}$cm$^{-3}$ to $10^{17}$cm$^{-3}$. The J-V plots for different bulk defect densities of the DPSC and the evolution of performance parameters of the DPSC with increase of the bulk defect density are presented in figure 2 and figure 3. The PV parameters of the Cs$_2$TiBr$_6$ DPSC are listed in Table 2.

From figure 2 and figure 3, we can see that the open-circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$) and fill factor (FF) remain constant at the beginning and then decrease rapidly when the bulk defect density increases to more than $10^{13}$cm$^{-3}$. The trend is due to the small, almost negligible effect on photo-generated carriers when the bulk defect density is below the threshold ($10^{13}$cm$^{-3}$). In contrast, the limiting effect on photo-generated carriers is dramatically increased when the bulk defect density is larger than the threshold ($10^{13}$cm$^{-3}$). When the bulk defect density increases above this threshold, the photo-generated carriers of light in the absorber layer are more easily trapped by the bulk defects resulting in an overall decrease in the $V_{oc}$, $J_{sc}$, and FF. Due to the above facts, the PCE remains constant at 9.97% when the bulk defect density is less than $10^{13}$cm$^{-3}$ and then starts to decrease after the bulk defect density exceeds $10^{13}$cm$^{-3}$, reaching a minimum value of 2.47% at $10^{17}$cm$^{-3}$. Therefore, we choose the threshold of $10^{13}$cm$^{-3}$ as the optimal bulk defect density, and the corresponding cell parameters are $V_{oc}$ of 0.94 V, $J_{sc}$ of 12.57 mA/cm$^2$, FF of 84.57%, and PCE of 9.97%.

![Figure 2. J-V plots for different bulk defect densities of the Cs$_2$TiBr$_6$ DPSC.](image-url)
Figure 3. (a) Evolution of Voc and Jsc of the DPSC with increase of the bulk defect density; (b) Evolution of PCE and FF of the DPSC with increase of the bulk defect density.

Table 2. PV parameters of the Cs₂TiBr₆ DPSC with increase of the bulk defect density.

| Defect Density (cm⁻³) | Voc (V) | Jsc (mA/cm²) | FF (%) | PCE (%) |
|-----------------------|---------|--------------|--------|---------|
| 10¹¹                  | 0.94    | 12.57        | 84.57  | 9.97    |
| 10¹²                  | 0.94    | 12.57        | 84.57  | 9.97    |
| 10¹³                  | 0.94    | 12.57        | 84.57  | 9.97    |
| 10¹⁴                  | 0.94    | 12.50        | 84.57  | 9.90    |
| 10¹⁵                  | 0.94    | 11.84        | 84.51  | 9.37    |
| 10¹⁶                  | 0.93    | 8.17         | 83.76  | 6.33    |
| 10¹⁷                  | 0.90    | 3.41         | 80.32  | 2.47    |

4. Conclusion
We simulate the DPSC with the FTO/ SnO₂/ Cs₂TiBr₆/ PEDOT:PSS/ Au structure. By using SCAPS-1D simulation software, we investigate the effect of the bulk defect density in the Cs₂TiBr₆ absorber layer for the performance of the Cs₂TiBr₆ DPSC. The conclusion is that there is a threshold value for the bulk defect density, the effect of bulk defects on performance is small and almost negligible when the defect density is less than the threshold value; the bulk defects will significantly reduce the performance of the DPSC when the defect density is more than the threshold value. We choose the threshold of 10¹³cm⁻³ as the optimal bulk defect density, and the corresponding DPSC has Voc of 0.94 V, Jsc of 12.57 mA/cm², FF of 84.57%, and PCE of 9.97%. Our numerical simulation results show that the Cs₂TiBr₆ DPSC has excellent potential and appropriate defect passivation is conducive for improving its performance.

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