

Article

Performance Optimization of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ Inorganic Perovskite Solar Cells with Gradient Bandgap

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Abstract: In recent years, inorganic perovskite solar cells (PSCs) based on CsPbI_3 have made significant progress in stability compared to hybrid organic–inorganic PSCs by substituting the volatile organic component with Cs cations. However, the cubic perovskite structure of $\alpha\text{-CsPbI}_3$ changes to the orthorhombic non-perovskite phase at room temperature resulting in efficiency degradation. The partial substitution of an I ion with Br ion benefits for perovskite phase stability. Unfortunately, the substitution of Br ion would enlarge bandgap reducing the absorption spectrum range. To optimize the balance between band gap and stability, introducing and optimizing the spatial bandgap gradation configuration is an effective method to broaden the light absorption and benefit the perovskite phase stability. As the bandgap of the $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite layer can be adjusted by I–Br composition engineering, the performance of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ based PSCs with three different spatial variation Br doping composition profiles were investigated. The effects of uniform doping and gradient doping on the performance of PSCs were investigated. The results show that bandgap (E_g) and electron affinity(χ) attributed to an appropriate energy band offset, have the most important effects on PSCs performance. With a positive conduction band offset (CBO) of 0.2 eV at the electron transport layer (ETL)/perovskite interface, and a positive valence band offset (VBO) of 0.24 eV at the hole transport layer (HTL)/perovskite interface, the highest power conversion efficiency (PCE) of 22.90% with open-circuit voltage (V_{OC}) of 1.39 V, short-circuit current (J_{SC}) of 20.22 mA/cm^2 and filling factor (FF) of 81.61% was obtained in uniform doping $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ based PSCs with $x = 0.09$. By carrying out a further optimization of the uniform doping configuration, the evaluation of a single band gap gradation configuration was investigated. By introducing a back gradation of band gap directed towards the back contact, an optimized band offset (front interface CBO = 0.18 eV, back interface VBO = 0.15 eV) was obtained, increasing the efficiency to 23.03%. Finally, the double gradient doping structure was further evaluated. The highest PCE is 23.18% with V_{OC} close to 1.44 V, J_{SC} changes to 19.37 mA/cm^2 and an FF of 83.31% was obtained.

Keywords: $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$; inorganic perovskite solar cells; gradient doping; SCAPS



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1. Introduction

Organic–inorganic perovskite solar cells (PSCs) have simpler a manufacturing process, lower cost and higher theoretical efficiency than silicon-based solar cells [1]. They also have an excellent optical absorption capacity ($>700\text{ nm}$) [2], high absorption coefficients ($10^4\sim 10^5\text{ cm}^{-1}$) [3], high carrier mobility ($>100\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [4], long diffusion lengths ($10^2\sim 10^3\text{ nm}$) [5] and low exciton binding energy ($\approx 26\text{ meV}$) [6]. Over the past decade, the efficiency of perovskite solar cells has increased from 3.9% to 25.73% [7,8], but the photo-instability and thermal instability of organic–inorganic perovskite solar cells have also restricted the commercialization of perovskite solar cells [9–12].

In recent years, cesium-based perovskite solar cells have attracted extensive attention because of their inorganic stability and outstanding light absorption capacity [13–16]. Inorganic halogen perovskite solar cells CsPbX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) have high thermal stability [17,18], and the highest efficiency of inorganic halogen perovskite solar cells based on CsPbI_3 has reached 21.14% [19]. However, the black phase of the cubic perovskite structure $\alpha\text{-CsPbI}_3$, whose bandgap (E_g) is 1.68 eV, is unstable at room temperature because of the small tolerance factor [20]. It converts to a non-perovskite phase of $\delta\text{-CsPbI}_3$ ($E_g = 2.8$ eV), which is an indirect band gap semiconductor [14,21], resulting in a weakened optical absorption capacity. By incorporating an appropriate Br element concentration into CsPbI_3 to form $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$, the tolerance factor can be effectively improved, reducing the $\alpha\text{-CsPbI}_3$ formation temperature and the defect formation which can effectively inhibit non-radiative recombination to improve open-circuit voltage [22,23].

As $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ PSCs can obtain a suitable bandgap by adjusting the I–Br ratio to achieve spectral response conditions and can be better combined with solar cells of other materials, inorganic perovskite is one of the candidate materials for tandem solar cells. In recent years, further improving the conversion efficiency of inorganic perovskite tandem solar cells has been an important research topic. At present, $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ all-inorganic PSCs as the bottom cell of the layered solar cell have an efficiency of 23.21% [24], higher than the efficiency of single all-inorganic PSCs. The maximum efficiency of single-junction $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ PSCs can reach 21.14% [19]. The maximum efficiencies of CsPbI_2Br , CsPbIBr_2 , and CsPbBr_3 are 17.8% [25], 12.05% [26] and 11.08% [27], respectively. With the increase in Br content, the efficiency of all-inorganic PSCs continuously decreases. Because E_g increases and larger energy band offset with the increase of Br content lead to a decrease in the optical absorption range.

The advantage of the gradient bandgap structure is that it can optimize the interface energy offset. The gradient bandgap structure can be used to set different doping concentrations on both sides of the material, ensuring that each interface can obtain a better energy band alignment. At the same time, a built-in electric field can be formed within the absorption layer. The appropriate direction of the built-in electric field can promote the transfer of carriers, further improving the efficiency of PSCs. To further optimize the performance of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ PSCs, we attempt to introduce a gradient bandgap structure into $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ PSCs to optimize the energy band and improve the open-circuit voltage.

In addition, while the organic hole transport layer can enable high efficiency in devices, the organic hole transport material (HTM) is prone to decomposition and typically requires additives (such as bistrifluoromethanesulfonimide lithium salt (LiTFSI) and Tributyl phosphate (TBP)) to assist, which can exacerbate device instability [28]. Therefore, this article first attempts to optimize the organic hole transport layer (HTL) by selecting a suitable HTM to improve device stability and reduce costs. Secondly, the influence of parameters of the uniform doping absorption layer on the performance of PSCs is analyzed. Finally, the gradient bandgap $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ PSCs are established to optimize the cell performance.

2. Device Simulation

The schematic structure of the simulated perovskite solar cell in this study is illustrated in Figure 1 as $\text{Au}/\text{Spiro-OMeTAD}/\text{CsPbI}_3/\text{TiO}_2/\text{FTO}$ using SCAPS which is a one dimensional solar cell simulation program developed by the University of Gent, Belgium. The thickness of each layer material is as follows: 170 nm 2,2',7,7'-Tetrakis [N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD), 750 nm CsPbI_3 , 25 nm compact-titanium dioxide (c- TiO_2) and 300 nm fluorine-doped tin oxide (FTO). In detail, Au was used as a back contact, Spiro-OMeTAD as a p-type hole transport layer. CsPbI_3 as a p-type absorber layer and c- TiO_2 as an n-type buffer layer. FTO, as the front contact electrode, is a type of fluorine-doped SnO_2 transparent conductive glass. Considering the interface recombination, two interface defect layers (IDLs) between the HTL/absorber layer and the electron transfer layer (ETL)/absorber layer, named IDL1 and IDL2, were considered in the simulated device. The Lambert Beer model was chosen as the optical

model. Standard AM1.5G was used for incident spectrum. The incident light entered from the FTO side. Under illumination, we can calculate the open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), fill factor (FF), power conversion efficiency (PCE) and other parameters, such as the current-voltage (J-V) characteristic curve and spectral response.

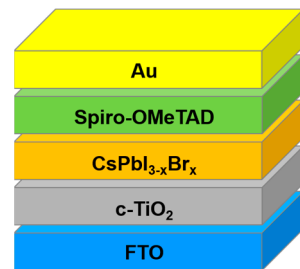


Figure 1. Schematic structure of the simulated perovskite solar cell.

Table 1 shows the main parameters of the materials in the model [29–36]. The series resistance and shunt resistances were set to $3 \Omega\text{cm}^2$ and $2150 \Omega\text{cm}^2$, respectively. The electron and hole thermal velocities in each layer were set to 10^7 cm/s . The optical absorption coefficient (α) curve can be calculated by the equation $\alpha = A_\alpha (h\nu \cdot E_g)^{1/2}$, where $A_\alpha = 10^5$. Apart from IDL1 and IDL2 having higher defect concentrations ($N_t = 10^{15} \text{ cm}^{-3}$), the other parameters of IDL1 and IDL2 were consistent with the absorption layer. The defect type was neutral. The defect distribution type of the absorption layer was Gaussian distribution. The defect distribution type of the other layers was single. The variation of each parameter in the absorbing layer is dependent on the value of x in $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$. The linear law is shown below, where the parameters of CsPbI_3 , CsPbBr_3 and $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ were assumed to be P_I , P_{Br} and P_{diop} , respectively:

$$P_{diop} = P_I(1 - x) + P_{Br} \quad (1)$$

Table 1. Main parameters of perovskite solar cell [29–36].

Parameter Name	Spiro-OMeTAD	CsPbI ₃	Composition Dependence Law	CsPbBr ₃	TiO ₂	FTO
Thickness d (nm)	170	750	Uniform	750	25	300
Bandgap energy E_g (eV)	3	1.68	Linear	2.3	3.2	3.5
Electron affinity χ (eV)	2.45	3.95	Cubic equation	3.3	3.9	3.9
Relative permittivity ϵ_r	3	10	Linear	7.3	9	9
Effective conduction band density N_C (cm^{-3})	2.2×10^{18}	2.2×10^{18}	Logarithmic	1×10^{19}	1×10^{21}	1×10^{21}
Effective valance band density N_V (cm^{-3})	1.8×10^{19}	1.8×10^{19}	Logarithmic	1×10^{19}	2×10^{20}	1.8×10^{20}
Electron mobility μ_n ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	2×10^{-4}	30	Linear	10	20	20
Hole mobility μ_p ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	2×10^{-4}	30	Linear	10	10	10
Donor concentration N_D (cm^{-3})	-	-	-	-	1×10^{18}	2×10^{19}
Acceptor concentration N_A (cm^{-3})	2×10^{18}	1×10^{15}	Uniform	1×10^{15}	-	-
Defect density N_t (cm^{-3})	1×10^{15}	2.07×10^{14}	Logarithmic	1.58×10^{13}	1×10^{15}	1×10^{15}

The logarithmic law is shown below:

$$P_{diop} = P_I^{(1-x)} \times P_{Br}^x \quad (2)$$

The simulated perovskite solar cell structure is based on the experimental literature of Yuqi Cui et al. [19]. In order to confirm the reliability of the device parameters used in this work, the simulated J-V characteristic were compared to the experimental result of the perovskite solar cell reported in reference [19] firstly. Figure 2 shows the simulated result comparing to the experimental data. The results of the J-V characteristic curve are similar to the result reported in the experimental literature [19] with $V_{OC} = 1.25$ V, $J_{SC} = 21.61$ mA/cm², FF = 78.13%, and PCE = 21.18%, indicating that the simulation parameters used in this paper are valid.

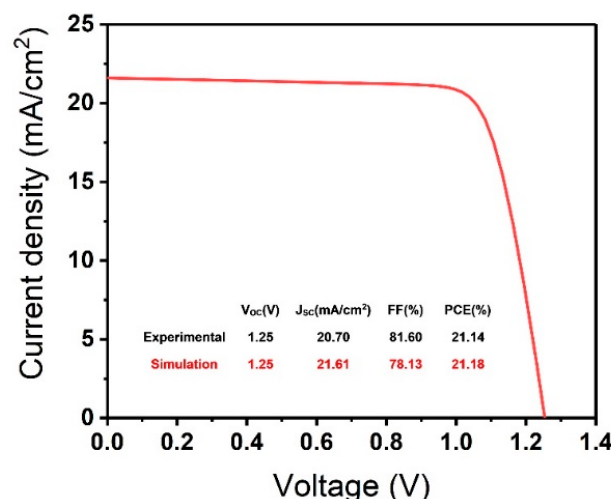


Figure 2. Comparison between experimental and simulation results.

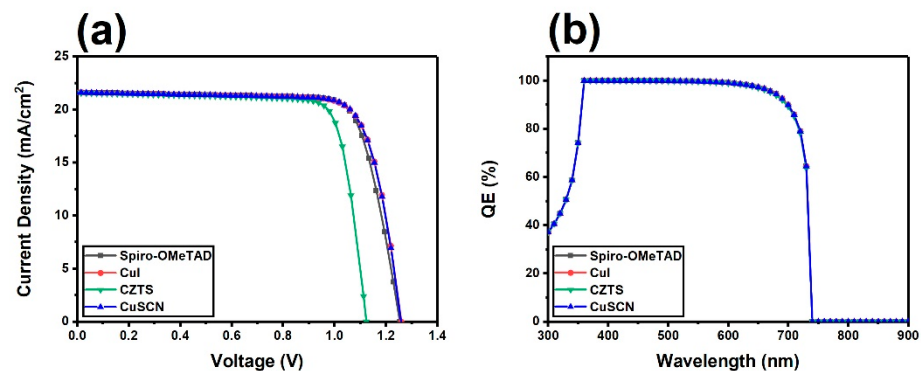
3. Results and Discussion

3.1. Influence of the Hole Transport Layer on Device Performance

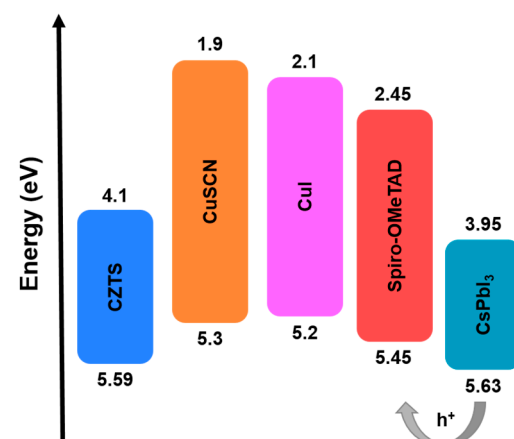
In this section, we compare several commonly used inorganic HTMs and attempt to replace Spiro-OMeTAD. The material parameters used in this section are shown in Table 2 [37–40]. Figure 3 shows the J-V curves and quantum efficiency (QE) of different HTMs. Meanwhile, the computational results of various materials are shown in Table 3. By comparison, we can find that different HTMs have little effect on QE. This is because HTL is located on the back of the solar cell, so HTL has a relatively small impact on light absorption. The energy band plot (Figure 4) shows a good band arrangement between the valence band of the CsPbI₃ and the highest occupied molecular orbital (HOMO) of all hole transport materials. By comparison, we can see that CZTS has the lowest V_{OC} (1.12 eV), which is due to the narrow bandgap of CZTS. Therefore, CZTS is not an ideal material for CsPb(I_{1-x}Br_x)₃ PSCs. Spiro-OMeTAD, CuI, and CuSCN exhibit similar efficiencies (21.18%, 21.22% and 21.25%, respectively). Although Spiro-OMeTAD and CuSCN have better band alignment than CuI, both of them have the drawbacks of being expensive and having low conductivity. Meanwhile, serious mutual diffusion between CuSCN and the absorber layer restricts the further performance improvement of the device [41]. CuI has better conductivity, higher carrier mobility and lower cost, so in the following work, CuI will replace Spiro-OMeTAD as the HTM.

Table 2. Material parameters of the proposed HTL [37–40].

Parameter Name	Spiro-OMeTAD	CuI	CuSCN	CZTS
Thickness d (nm)	170	170	170	170
Bandgap energy E_g (eV)	3	3.1	3.4	1.49
Electron affinity χ (eV)	2.45	2.1	1.9	4.1
Relative permittivity ϵ_r	3	6.5	10	7
Effective conduction band density N_C (cm^{-3})	2.2×10^{18}	2.8×10^{19}	1.7×10^{19}	2.5×10^{20}
Effective valance band density N_V (cm^{-3})	1.8×10^{19}	1×10^{19}	1.8×10^{18}	2.5×10^{20}
Electron mobility μ_n ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	2×10^{-4}	100	100	25
Hole mobility μ_p ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	2×10^{-4}	43.9	25	20
Donor concentration N_D (cm^{-3})	-	-	-	-
Acceptor concentration N_A (cm^{-3})	2×10^{18}	1×10^{20}	1×10^{18}	1.7×10^{18}
Defect density N_t (cm^{-3})	1×10^{15}	1×10^{15}	1×10^{15}	1×10^{15}

**Figure 3.** (a) J-V curves and (b) QE of different hole transport materials.**Table 3.** Cell performance of different HTMs.

Materials	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
Spiro-OMeTAD	1.25	21.61	78.13	21.18
CuI	1.26	21.61	77.94	21.22
CuSCN	1.26	21.61	78.09	21.25
CZTS	1.12	21.56	80.68	19.55

**Figure 4.** Band alignment between CsPbI₃ and different HTLs.

3.2. Influence of CsPbI₃ Perovskite Layer Parameters on Device Performance

For the CsPbI₃ absorption layer, the band gap (E_g), electron affinity (χ), dielectric constant (ϵ_r), conduction band effective density of states (N_C), valence band effective density of states (N_V), electron mobility (μ_n), hole mobility (μ_p), defect density (N_t) and other parameters of the material will change after doping with the Br element, and the influence of these parameters on the device performance is also different. Therefore, this section simulates the influence of each parameter on the device performance.

Figure 5 illustrates the relationship between device performance and various parameters, including thickness, N_C , N_V and N_t . As shown in Figure 5a,b, J_{SC} increases with increasing thickness. The reason is that the absorbing layer can capture more photons, generating more electron–hole pairs, and increasing J_{SC} . However, this also increases the series resistance and internal energy consumption, leading to a decrease in V_{OC} and FF. When the thickness is too high, the device efficiency growth slows down. The reason is that the series resistance will further increase and more carrier recombination will occur, resulting in an increase in the recombination current. This also explains why J_{SC} increases slowly. Moreover, too thick an absorbing layer will increase manufacturing costs, so the thickness should be controlled within approximately 750 nm. As shown in Figure 5c,d, an excessive doping concentration can lead to more charge carriers being trapped by defects, resulting in a decrease in V_{OC} with increasing doping concentration. Due to the increase in doping concentration, scattering and recombination increase, suppressing hole transport. Therefore, selecting an appropriate doping concentration can improve the performance of the cell. Considering the increase in cost caused by too low doping, N_t should be kept within 10^{14} cm^{-3} in industrial production.

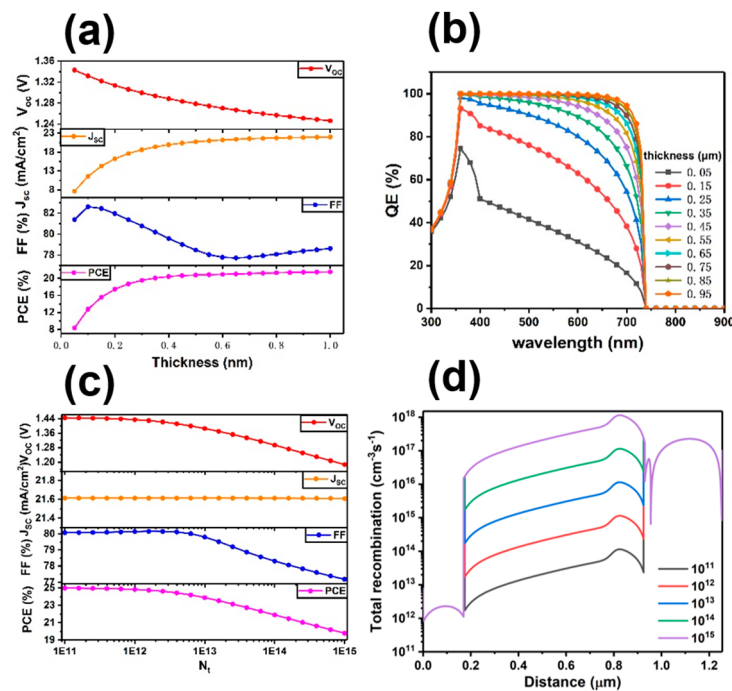


Figure 5. Influence of different parameters on cell performance: (a) thickness and (c) N_t ; (b) effect of thickness on QE and (d) effect of N_t on total recombination.

As shown in Figure 6a,b, with an increase in N_C , the Fermi level decreases, which leads to a reduction in the built-in electric field within the absorption layer. This reduction is detrimental to the separation of charge carriers at the interface, resulting in an increase in recombination current and a decrease in V_{OC} . As shown in Figure 6c,d, N_V has a similar effect on cell performance to N_C . With an increase in N_V density, the Fermi level rises, which leads to a reduction in the built-in electric field within the absorption layer. This

reduction is detrimental to the separation of charge carriers at the interface, resulting in an increase in recombination current and a decrease in V_{OC} .

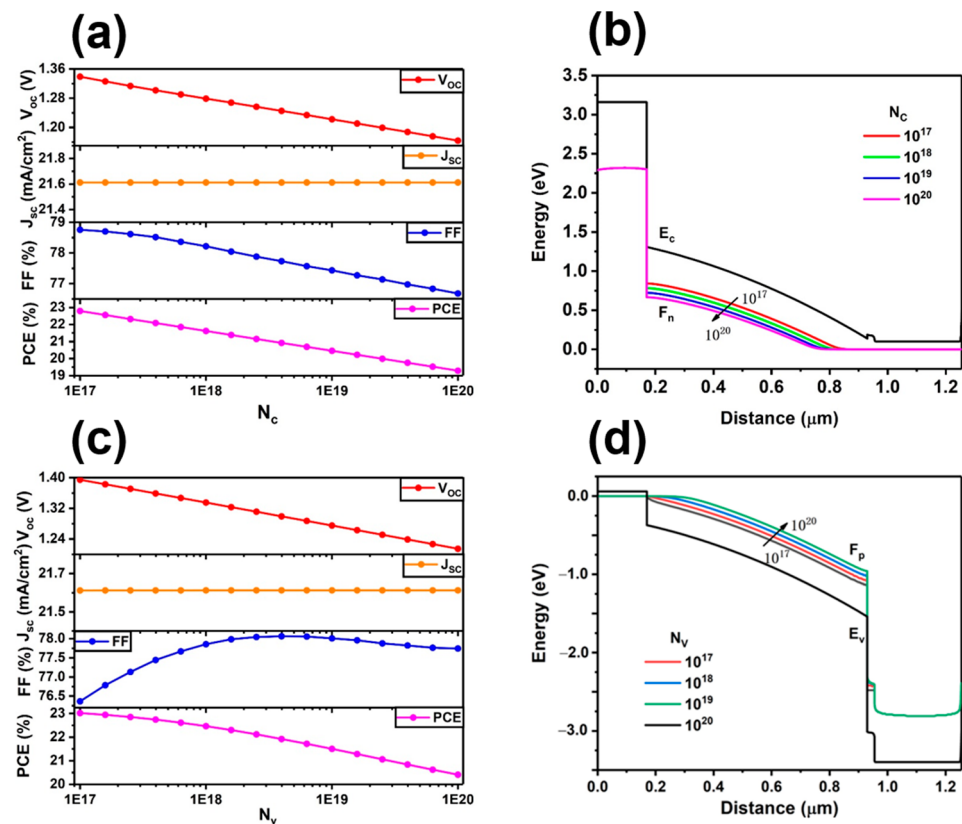


Figure 6. Influence of different parameters on battery performance: (a) N_c and (c) N_v ; (b) effect of N_c on conduction band Fermi level (F_n) and (d) effect of N_v on valence band Fermi level (F_p).

In addition to the above parameters, E_g and χ have a more significant impact on PSCs performance. Figure 7 shows the effect of E_g and χ on PSCs performance. The maximum PCE is 22.12% when E_g is 1.68 eV and χ is 3.78 eV. However, not every pair of E_g – χ data can be implemented in experiment. There is a fixed correspondence between them. Therefore, such high-efficiency doping cannot be achieved in the experiment. As shown in Figure 7, the increase in E_g leads to the increase in V_{OC} . At the same time, because the wider bandgap is not conducive to the light absorption (Figure 8a), the photon-generated carrier will be greatly reduced, resulting in a sharp decline in J_{SC} , and thus the reduction of cell efficiency. The change of E_g and χ will lead to band offset, which is another cause of PSCs performance change (Figure 8b). Take the valence band as an example, when $E_g = 1.68$ eV and $\chi = 3.4$ eV, the valence band of HTL is lower than the absorption layer and a “spike” will be formed at the interface. When $E_g = 1.68$ eV and $\chi = 3.8$ eV, the valence band of the hole layer is higher than that of the absorption layer, and a “cliff” will be formed at the interface. Excessive band offset will hinder carrier diffusion and lead to the incomplete depletion of the absorption layer. The carrier cannot be collected during its lifetime, leading to the increase in carrier recombination rate. Therefore, suitable E_g and χ can optimize the energy band at the interface and improve the PSCs’ efficiency.

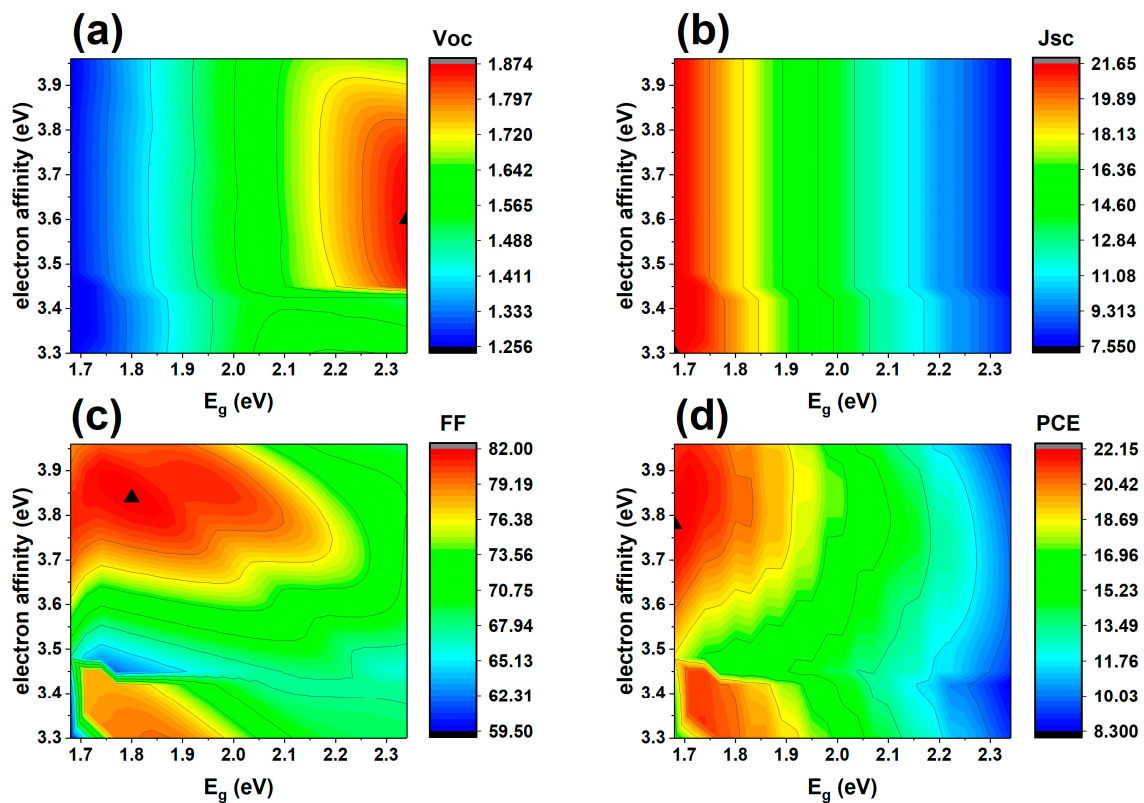


Figure 7. Influence of bandgap and electron affinity on PSCs: (a) V_{OC} , (b) J_{SC} , (c) FF and (d) PCE.

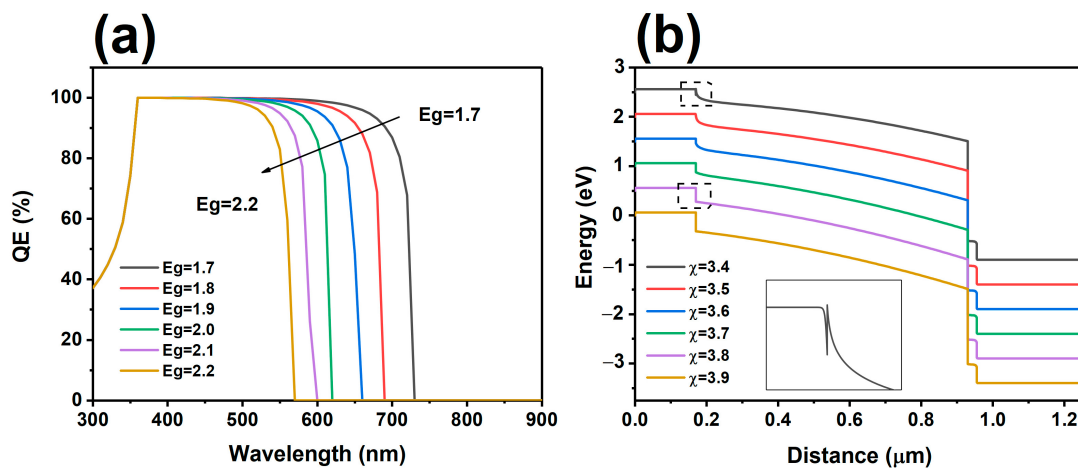


Figure 8. Influence of (a) bandgap on QE and (b) electron affinity on valence band.

3.3. Uniform Composition Configuration

The energy band of the absorption layer $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ is closely related to the x value. According to the experimental results of Yuanzhi Jiang et al. [42], the variation curves of the conduction and valence bands of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ with x value can be obtained by polynomial fitting (Figure 9) [42–45]. It can be seen from Figure 9 that with the increase in Br content, both the bottom of the conduction band and the top of the valence band first increase and then decrease before increasing again, but E_g keeps increasing. The relationship between x values in the $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ absorption layer in this model and other parameters (energy band, ϵ_r , N_C , N_V , μ_n and μ_p) has been shown in Table 1. As shown in Figure 10, the effect of Br content change on the performance of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ PSCs is simulated here. The results show that when $x = 0$, the efficiency of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite solar cells

reaches 21.22%, V_{OC} is 1.26 V, J_{SC} is 21.26 mA/cm² and FF is 77.94%. When the x value gradually increases, the efficiency increases first, and reaches the maximum when $x = 0.09$, $V_{OC} = 1.39$ V, $J_{SC} = 20.22$ mA/cm², FF = 81.61% and PCE = 22.9%, and then the efficiency starts to diminish. One reason is that an excessive energy band results in a reduced light absorption range, which in turn leads to a decrease in J_{SC} (Figure 11).

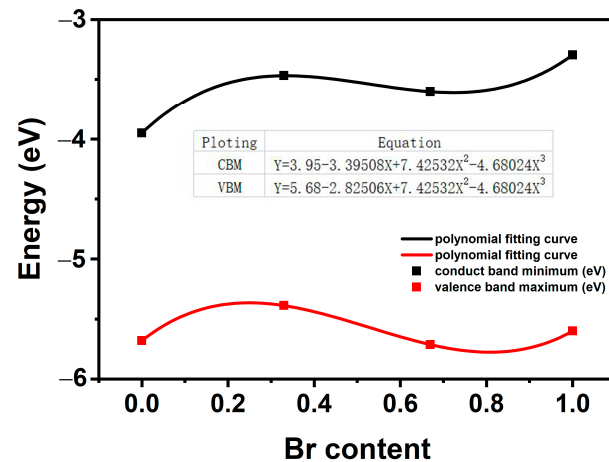


Figure 9. The energy band of $CsPb(I_{1-x}Br_x)_3$ varies with the x value [42–45].

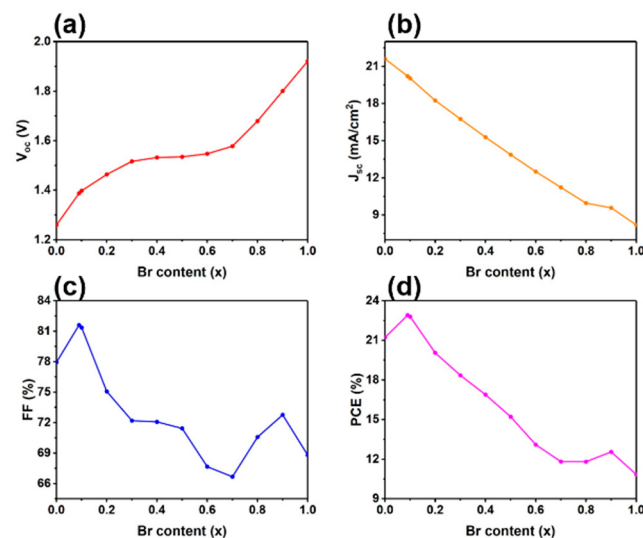


Figure 10. Influence of uniform doping on PSCs: (a) V_{OC} , (b) J_{SC} , (c) FF and (d) PCE.

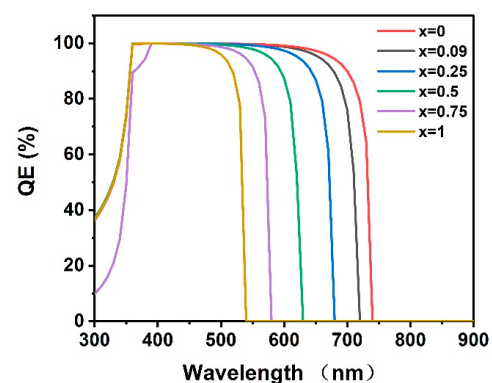


Figure 11. Effect of uniform doping on QE.

The other reason is that when $x = 0.09$, the valence band offset (VBO) is 0.24 eV (Figure 12a), and the conduction band offset (CBO) is 0.2 eV (Figure 12b). The band offset is significantly better than $x = 0.25, 0.5, 0.75$ and 1. Compared with $x = 0$, although CBO (-0.05 eV) increased, VBO (0.43 eV) decreased significantly. This makes the band offset close to a reasonable range of 0–0.2 eV [46]. Therefore, the band matching is better when $x = 0.09$, effectively reducing the carrier recombination rate inside the cell (Figure 12c), and the PSCs efficiency reaches the maximum.

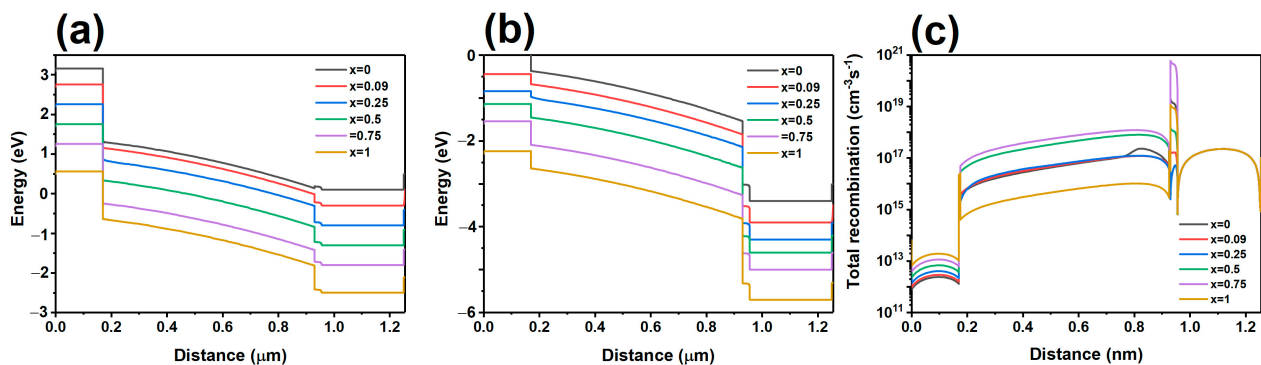


Figure 12. Effect of uniform doping on (a) conduction band, (b) valence band and (c) total recombination.

3.4. Gradient Composition Configuration

Gradient doping can effectively improve the photoelectric conversion efficiency of perovskite solar cells. Therefore, a similar doping method is applied to $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite solar cells in this study. Figure 13 shows two different types of gradient doping. The Br doping density of the $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ absorption layer is controlled by the depth. The x value changes linearly with the depth, so that the energy band changes accordingly. The E_g increases with the increase in the x value, when the Br content of the absorption layer/ETL (X_f) is higher than the Br content of the absorption layer/HTL (X_b). This is called the pre-segregation structure; otherwise, it is called the post-segregation structure.

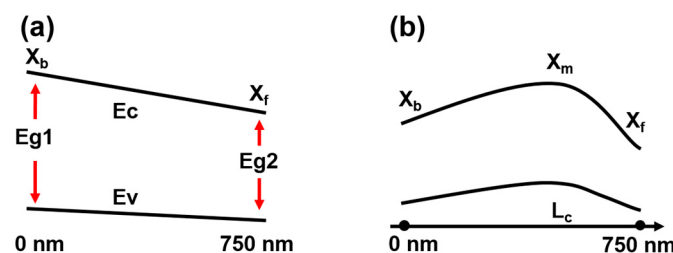


Figure 13. Two gradient doping types: (a) single-gradient doping and (b) double-gradient doping.

When X_b is unchanged, the cell performance will gradually decay with the increase in X_f . This is because with the increase in X_f , the band gap of the absorption layer at the $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3/\text{ETL}$ interface gradually increases, forming a pre-segregation structure, thus generating a built-in electric field in the absorption layer in the opposite direction, which is not conducive to the collection of carriers and aggravates the recombination of carriers. An increase in the reverse saturation current leads to a decrease in the conversion efficiency.

The black icon marked in Figure 14 is the position corresponding to the simulated optimal cell efficiency. When $X_b = 0.17$ and $X_f = 0.08$, the cell performance reaches its best, and V_{OC} is 1.39 V, J_{SC} is 20.22 mA/cm^2 , FF is 82.12%, and PCE is 23.03%. At this time, the bandgap of the rear interface $E_{g1} = 1.79$ eV, and the bandgap of the front interface $E_{g2} = 1.73$ eV. The conduction band and valence band gradually rise from the front interface to the back interface, forming a post-segregation structure. A built-in electric field in the same direction is formed within the absorption layer, which enhances carrier separation, promotes carrier collection and reduces recombination, thus improving cell performance.

Compared with uniform doping, QE decreases in single gradient doping (Figure 15a), which is because the increase in E_g makes carrier separation more difficult and reduces the light absorption capacity. Figure 15b shows the energy band after translation, and we calculated that the CBO of single gradient doping is 0.18 eV, and VBO is 0.15 eV. The CBO of uniform doping is 0.2 eV and VBO is 0.24 eV. The smaller band offset leads to a decrease in the carrier recombination rate (Figure 15c).

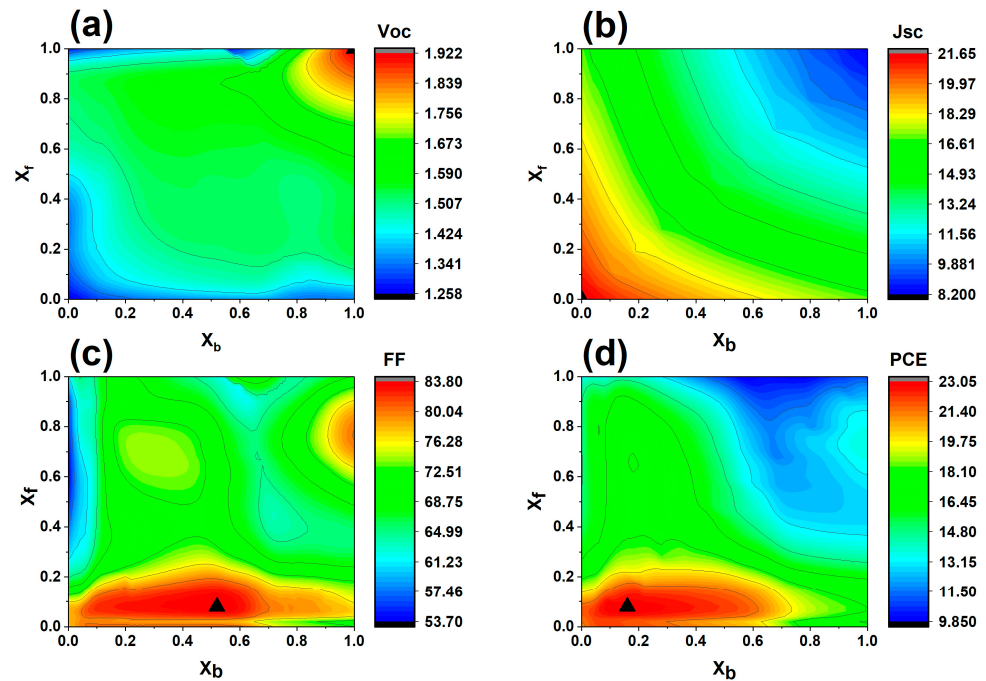


Figure 14. Influence of single gradient doping on PSCs: (a) V_{OC} , (b) J_{SC} , (c) FF and (d) PCE.

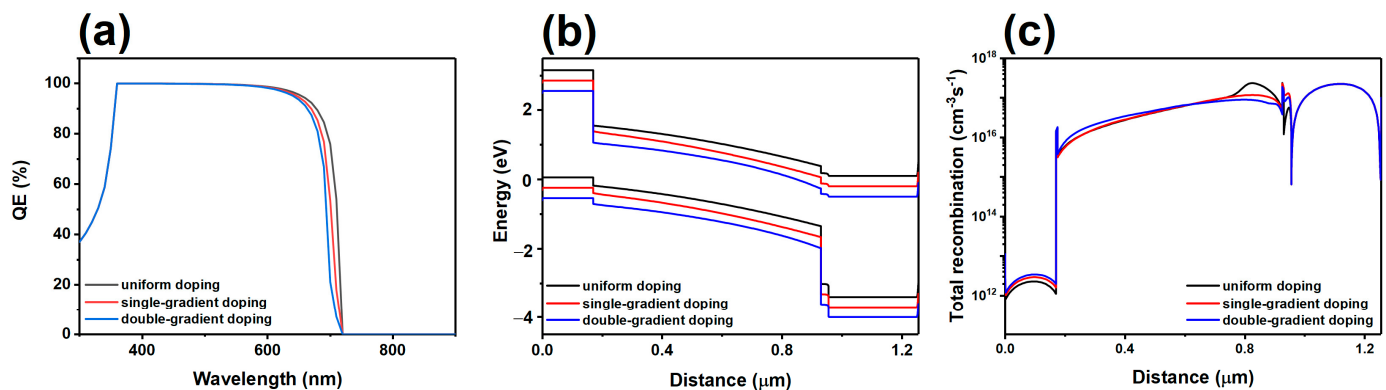


Figure 15. Influence of different doping types on (a) QE, (b) energy gap and (c) total recombination.

Jiang Jie et al. proposed a double-gradient doping structure to optimize cell performance [47]. This kind of band structure is concave, high on both sides and low in the middle, which can improve J_{SC} . This structure is applied to the $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ absorption layer (Figure 13b). A more appropriate band gap near the front surface of the absorption layer can improve carrier transfer efficiency. X_f , X_b , L_c and X_m represent the Br doping concentration on the front surface, the Br doping concentration on the back surface, the doping depth, and the maximum or minimum Br doping concentration inside the absorption layer, respectively. The impact of X_b and X_f on PSCs' performance has been discussed previously. Figure 16 shows the effect of L_c and X_m on PSCs performance. When $X_f = 0.07$, $X_b = 0.15$, $L_c = 600$ nm and $X_m = 0.17$, PSCs performance reaches its highest ($V_{OC} = 1.44$ V, $J_{SC} = 19.37$ mA/cm², FF = 83.31% and PCE = 23.18%).

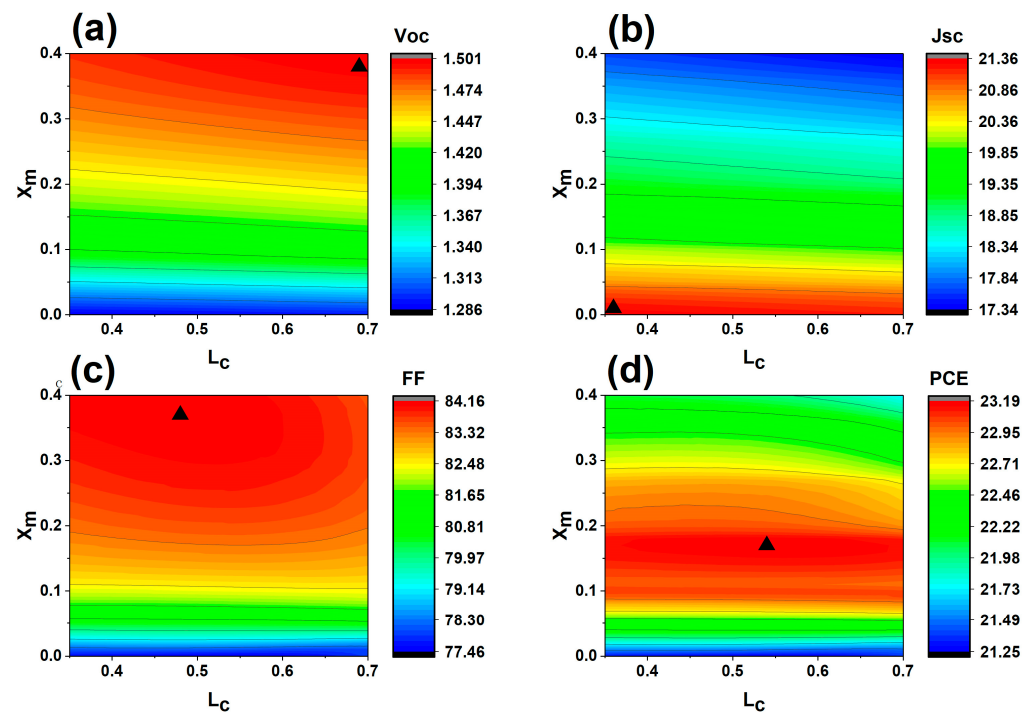


Figure 16. Influence of double gradient doping on PSCs: (a) V_{oc} , (b) J_{sc} , (c) FF and (d) PCE.

Comparing single-gradient doping with double-gradient doping, QE decreases slightly because the energy band is slightly larger (Figure 15a). The best efficiency of double-gradient doping is 0.15% higher than that of single-gradient doping. The improvement mainly focuses on the increase in V_{oc} by 0.05 eV, the decrease in J_{sc} by 0.85 mA/cm² and the increase in FF by 1.19%. This is contrary to the experimental results of Jiang Jie et al. One reason is that the sunlight is incident on the front interface, and the front interface concentrations of single-gradient doping and double-gradient doping are not much different, so the range of light absorption is almost constant. However, since the doping concentration of the absorption layer reaches the maximum ($X_m = 0.17$) when $L_c = 540$ nm, L_c is closer to the front interface (absorption layer/ETL), $E_g = 1.79$ eV. $X_b = 0.15$, $E_{g1} = 1.77$ eV, $X_f = 0.07$, $E_{g2} = 1.72$ eV. It can be seen that compared with single-gradient doping, the bandgap of double-gradient doping in the first half of the absorption layer (L_c —front interface) increases faster, while the bandgap of the second half (L_c —back interface) maintains a relatively high level. Previously, we analyzed that high bandgap would make it difficult for low-energy long-wavelength photons to be excited, so the absorption capacity of the absorption layer for long-wavelength light would be weakened (Figure 15a), and the number of electron–hole pairs generated would be reduced, thus leading to J_{sc} weakening. Another reason is that in the second half, due to the difference in bandgap, an electric field will be formed in an opposite direction of the in-built electric field, which has a negative effect on the transmission of carriers. It can be seen from Figure 16 that when $X_m < 0.07$ or $X_m > 0.25$, the cell efficiency drops sharply. The reason may be that too small a band gap will form a built-in electric field near the front surface in the direction opposite to the built-in electric field in the absorption layer, which will increase the carrier recombination rate at the interface, while too large a band gap will reduce light absorption. The CBO and VBO of double gradient doping are 0.15 eV and 0.15 eV respectively (Figure 15a,b). The band offset is decreased on the front surface, so the carrier recombination rate on the front surface is reduced. VBO remains unchanged (Figure 15c). So, the energy band is optimized to improve the efficiency.

4. Conclusions

In this paper, a more accurate energy band variation plot of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ PSCs was recovered, and SCAPS software was used to study and optimize the $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite solar cells with gradient bandgap. For the first time, we studied the effects of different HTM on PSCs performance, proving that a suitable HTL bandgap is important for PSCs performance, and selected CuI with a better carrier generation rate as the hole transport layer material. Second, we studied the influence of different parameters of the absorption layer on the PSCs performance. We find that the thickness of $\sim 750\text{nm}$ can improve the optical absorption capacity while taking into account the efficiency and cost. Too large N_C and N_V will cause the Fermi level to move away from conduction band and valence band, resulting in V_{OC} and efficiency loss. High N_t will lead to an increase in the carrier recombination rate, so N_t should be controlled within 10^{14} cm^{-3} . Thirdly, the influence of uniform doping on PSCs performance was studied. We find that when $x = 0.09$, there is a better matched band at HTM/perovskite interface ($V_{BO} = 0.24\text{ eV}$ and $C_{BO} = 0.2\text{ eV}$), with an efficiency of 22.90%. Finally, the influence of different types of gradient doping on PSCs performance was studied. Through the comparison, we find that although QE is slightly reduced by gradient doping, by adjusting the band, the band offset can be optimized ($C_{BO} = 0.18\text{ eV}$, $V_{BO} = 0.15\text{ eV}$), and a post-segregation structure can be formed to optimize carrier transport and increase efficiency ($PCE = 23.03\%$). The energy band is further optimized by double-gradient doping ($C_{BO} = 0.10\text{ eV}$, $V_{BO} = 0.15\text{ eV}$), and the efficiency is increased to 23.18%.

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