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# Electron extraction layer-driven performance enhancement in $\text{CaHfSe}_3$ photovoltaics

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Traditional solar cells – including those based on silicon or lead-halide perovskites – have a number of significant disadvantages, including long-term instability, costs, and toxicity. We demonstrate the suitability of  $\text{CaHfSe}_3$  as a promising next-generation lead-free thermally stable absorber material. We performed a comprehensive numerical simulation study using SCAPS-1D to consider several device topologies of the type FTO/ $\text{TiO}_2$  AZnO,  $\text{WS}_2/\text{CaHfSe}_3/\text{MoO}_3/\text{Au}$ , and to investigate the different features of a system based on  $\text{CaHfSe}_3$ . We conducted a full parametric study of the impacts of absorber thickness, defect density, acceptor doping and concentration, as well as carrier concentrations in the electron and hole transport layers. In addition, through experimentation we considered the operational characteristics of carrier generation-recombination methods, temperature and back contact effect current–voltage  $I$ – $V$  characteristics, quantum efficiency, and the influence of series and shunt resistance. This allowed us to determine the optimized configuration. The top-performing structure, FTO/ $\text{TiO}_2$ / $\text{CaHfSe}_3/\text{MoO}_3/\text{Au}$ , had an outstanding PCE of 32.39%,  $V_{\text{OC}} = 1.52$  V,  $J_{\text{SC}} = 23.17$  mA cm<sup>−2</sup>, and FF = 91.41%. This research offers both fundamental insights and practical guidance for developing stable, efficient, and environmentally friendly  $\text{CaHfSe}_3$ -based solar cells. It paves the path for further experimental realization and commercial application.

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## 1. Introduction

Transition to renewable energy sources has emerged as a global imperative to address the challenges posed by climate change and rising electricity demand. Among energy conversion technologies, solar cells have experienced significant growth thanks to advances in developing new semiconductor materials.<sup>1,2</sup> Although silicon-based photovoltaic cells currently dominate the market, they have certain limitations regarding manufacturing cost, efficiency, and stability. In particular, crystalline silicon suffers from intrinsic constraints as an indirect band gap semiconductor, its low absorption coefficient requires a minimum thickness to ensure sufficient light harvesting. Still, increasing thickness inevitably raises the series

resistance.<sup>3</sup> This trade-off between absorption and Joule losses fundamentally restricts the overall performance of silicon solar cells. These constraints have driven the exploration of alternative materials, especially perovskites, which are garnering increasing attention in this context due to their exceptional optical and electronic properties, cost-effectiveness, and sustainability for photovoltaic devices.<sup>4–6</sup> Specifically,  $\text{MAPbX}_3$  or  $\text{FABX}_3$  lead halide perovskites have demonstrated remarkable power conversion efficiency (PCE) of 27%.<sup>7</sup> However, conventional PSCs are weak in resilience to heat and humidity, have a high concentration of defects, are unstable due to the instability of organic cations, and contain poisonous lead (Pb), all of which pose significant health and environmental dangers, preventing their widespread commercialization. The primary obstacle is the search for lead (Pb)-free, stable, and eco-friendly materials. This is achieved by replacing cations such as  $\text{Ge}^{2+}$  or  $\text{Sn}^{2+}$ , which have advantageous band gaps, for  $\text{Pb}^{2+}$  ions.<sup>8,9</sup> However, the resultant perovskites are extremely unstable in air because of the strong oxidation propensity of  $\text{Ge}^{2+}$  and  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  and  $\text{Ge}^{4+}$ , respectively, which is linked to the increased energy levels of their respective 5s and 4s orbitals.<sup>10</sup> However, a major obstacle still stands in the way of these promising solar materials, poor durability.

This study is aimed at identifying materials with the positive attributes of lead halide perovskites while eliminating their

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disadvantages. Chalcogenide perovskites are one of the most promising alternatives due to their non-toxic nature, impressive structural stability, and good electronic properties. These compounds typically adopt the  $ABX_3$  structural formula, where A is an alkaline earth metal, B is a transition metal, and X is either sulfur (S) or selenium (Se).<sup>11</sup> A broad range of  $ABX_3$  chalcogenide perovskites was recognized by Sun *et al.* in 2015 as potential absorber materials for solar applications.  $BaZrS_3$ ,  $CaZrS_3$ ,  $SrZrS_3$ ,  $BaHfS_3$ ,  $CaHfS_3$ ,  $SrHfS_3$ ,  $CaTiS_3$ ,  $BaZrSe_3$ ,  $CaZrSe_3$ ,  $SrZrSe_3$ ,  $BaHfSe_3$ ,  $SrHfSe_3$ , and  $CaTiSe_3$  are some of the more prominent instances.<sup>12</sup> Simulations highlight the strong potential of  $ABX_3$ -based solar cells, but experimental realization is limited by the complexity of film growth and ambient stability issues, as defects and exposure to moisture or oxygen can reduce efficiency. Overcoming these challenges is essential to achieve the predicted performance. Crystalline chalcogenide perovskite (CP) thin films are typically synthesized at high temperatures, greater than 600 °C (1170 F), severely limiting the ability to fabricate both single and multi-junction solar cells. The production of high-quality CP films *via* physical deposition methods or chemical sulfidation processes typically involves temperatures as high as 700 to 1000 °C (1292 to 1832 F), where intermediate products frequently include

impurity phases in the final composition.<sup>13</sup> Additionally, fabricating CP thin films *via* solution-based methods remains a significant challenge, as no known solvent can withstand the extreme temperatures needed for their synthesis. Furthermore, in 2025, Hayes *et al.* devised a comprehensive method for synthesizing various  $ABS_3$  compounds, such as  $BaZrS_3$ ,  $BaTiS_3$ ,  $SrZrS_3$ , and  $SrHfS_3$ , together with colloidal phases synthesized within the Ba–Hf–S chemical system. These materials are composed of elements with a strong affinity for oxygen, notably group IV transition metals like Ti, Zr, and Hf.<sup>14</sup> This study identifies deficiencies in current research, noting that while  $BaZrS_3$  nanoparticles have been manufactured in various phases by colloidal techniques, a consistent procedure for orthorhombic perovskite nanoparticles has not been established. To solve this, the authors introduce a high-temperature hot-injection technique, which allows precise control over the formation of colloidal  $BaZrS_3$  nanoparticles, leading to a more reliable and scalable synthesis process. Recent studies on the  $ABS_3$  chalcogenide perovskite show that replacing S with Se dramatically lowers the bandgap moving it away from the visible to the near-infrared wavelength. This transformation improves the capability for photovoltaic implementation and appear more favorable for transitioning solar energy technology.<sup>15</sup> Hf based perovskites still suffer from bulk recombination mainly due to Hf vacancy defects.<sup>16</sup> The lead-free perovskite  $CaHfSe_3$  emerges as a viable alternative, as it combines the advantageous characteristics of semiconductors with properties comparable to its lead-based counterparts.

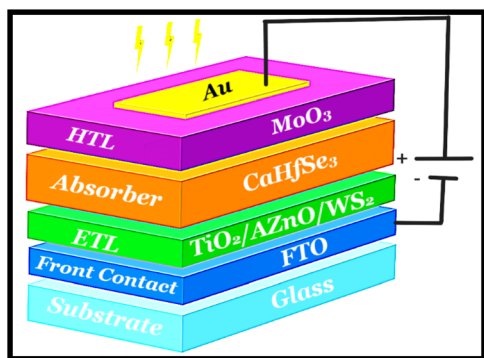


Fig. 1 The device architecture of the PSC based on  $CaHfSe_3$ .

Table 2 The contact work functions applied in the configurations

Metal contacts	Work function (eV) (ref. 8 and 18)
Cu	4.65
Fe	4.81
C	5
Au	5.1
Ni	5.5
Pt	5.7

Table 1 The key input values defining the architecture of the proposed solar cell

Parameters	FTO <sup>18</sup>	TiO <sub>2</sub> (ref. 16)	CaHfSe <sub>3</sub> (ref. 19)	WS <sub>2</sub> (ref. 20)	MoO <sub>3</sub> (ref. 21)	AZnO <sup>8</sup>
Thickness (μm)	0.1	0.03	Varied	0.03	0.03	0.03
Bandgap $E_g$ (eV)	3.5	3.33	1.65	1.8	3.17	3.33
Electron affinity $\chi$ (eV)	4	4.55	4	3.95	2.05	4.55
Dielectric permittivity (relative)	9	8.12	7.93	13.6	12.5	8.12
$N_c$ effective density of states in CB (cm <sup>-3</sup> )	$2.2 \times 10^{18}$	$4.1 \times 10^{18}$	$8.9 \times 10^{18}$	$1 \times 10^{18}$	$2.21 \times 10^{19}$	$4.1 \times 10^{18}$
$N_v$ effective density of states in VB (cm <sup>-3</sup> )	$1.8 \times 10^{19}$	$8.2 \times 10^{19}$	$1.1 \times 10^{19}$	$2.4 \times 10^{19}$	$1.8 \times 10^{19}$	$8.2 \times 10^{19}$
$V_{th,e}$ velocity of electrons (cm s <sup>-1</sup> )	$1 \times 10^7$	$1 \times 10^7$	$1 \times 10^7$	$1 \times 10^7$	$1 \times 10^7$	$1 \times 10^7$
$V_{th,p}$ velocity of holes (cm s <sup>-1</sup> )	$1 \times 10^7$	$1 \times 10^7$	$1 \times 10^7$	$1 \times 10^7$	$1 \times 10^7$	$1 \times 10^7$
$\mu_n$ mobility of electrons (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	20	100	18.77	100	25	100
$\mu_p$ mobility of holes (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	10	20	6.81	100	100	20
$N_D$ shallow uniform donor density (cm <sup>-3</sup> )	$21 \times 10^{19}$	$11 \times 10^{13}$	0	$1 \times 10^{18}$	0	$11 \times 10^{13}$
$N_A$ shallow uniform acceptor density (cm <sup>-3</sup> )	0	0	$1 \times 10^{19}$	0	$1 \times 10^{19}$	0
$N_t$ density of defect (cm <sup>-3</sup> )	$1 \times 10^{15}$	$1 \times 10^{17}$	$1 \times 10^{13}$	$1 \times 10^{15}$	$1 \times 10^{15}$	$1 \times 10^{17}$



These include favorable charge-carrier effective masses, a direct and optimal band gap, high absorption coefficients, and exceptional thermal stability, making it a promising absorber material for next-generation photovoltaics. The optical spectrum of the  $\text{CaHfSe}_3$  reports a clear absorption edge which corresponds to a direct electronic bandgap of 1.65 eV.<sup>15</sup> This optimization study of  $\text{CaHfSe}_3$ -based perovskite solar cells (PSCs) focuses on various combinations of electron and hole transport layers (ETL–HTL), using SCAPS-1D simulations, a one-dimensional solar cell modelling software based on capacitance. To enhance device performance,  $\text{MoO}_3$  is employed as the HTL in combination with  $\text{TiO}_2$ ,  $\text{WS}_2$ , and  $\text{AZnO}$  as ETL candidates. Key operational parameters such as back contact material, series resistance, and operating temperature are systematically examined. Additionally, the effects of absorber layer thickness and doping concentration are optimized to further improve cell efficiency. Analysis of current–voltage ( $J$ – $V$ ) characteristics and external quantum efficiency (EQE) confirms that the optimized configuration yields a significantly enhanced power conversion efficiency (PCE) compared to previously reported designs.

## 2. Device architecture and computational methodology

### 2.1. Numerical modeling technique

The numerical method employed in this research is based on simulations conducted with SCAPS-1D 3.3.11 (Solar Cell Capacitance Simulator – 1D), a widely used software for modeling the electrical behavior of thin-film solar cells, which solves the coupled Poisson's and continuity equations under steady-state conditions. As shown in eqn (1) Poisson equation, relates electrostatic potential to charge density in the material within the device:<sup>17</sup>

$$\frac{d^2\psi}{dx^2} = \frac{-q}{\epsilon} [p(x) - n(x) + N_D^+(x) - N_A^-(x) + p_t(x) - n_t(x)] \quad (1)$$

With  $\epsilon$ : dielectric constant,  $q$ : electron charge,  $\psi$ : electrostatic potential,  $n$ , and  $p$ : free electrons and holes,  $n_t$  and  $p_t$ : trapped electrons and holes,  $N_D^+$  and  $N_A^-$ : represent the densities of ionized donors and acceptors, respectively.

Poisson's equation must be solved in order to analyze solar cells since it shows how the electric potential is dispersed

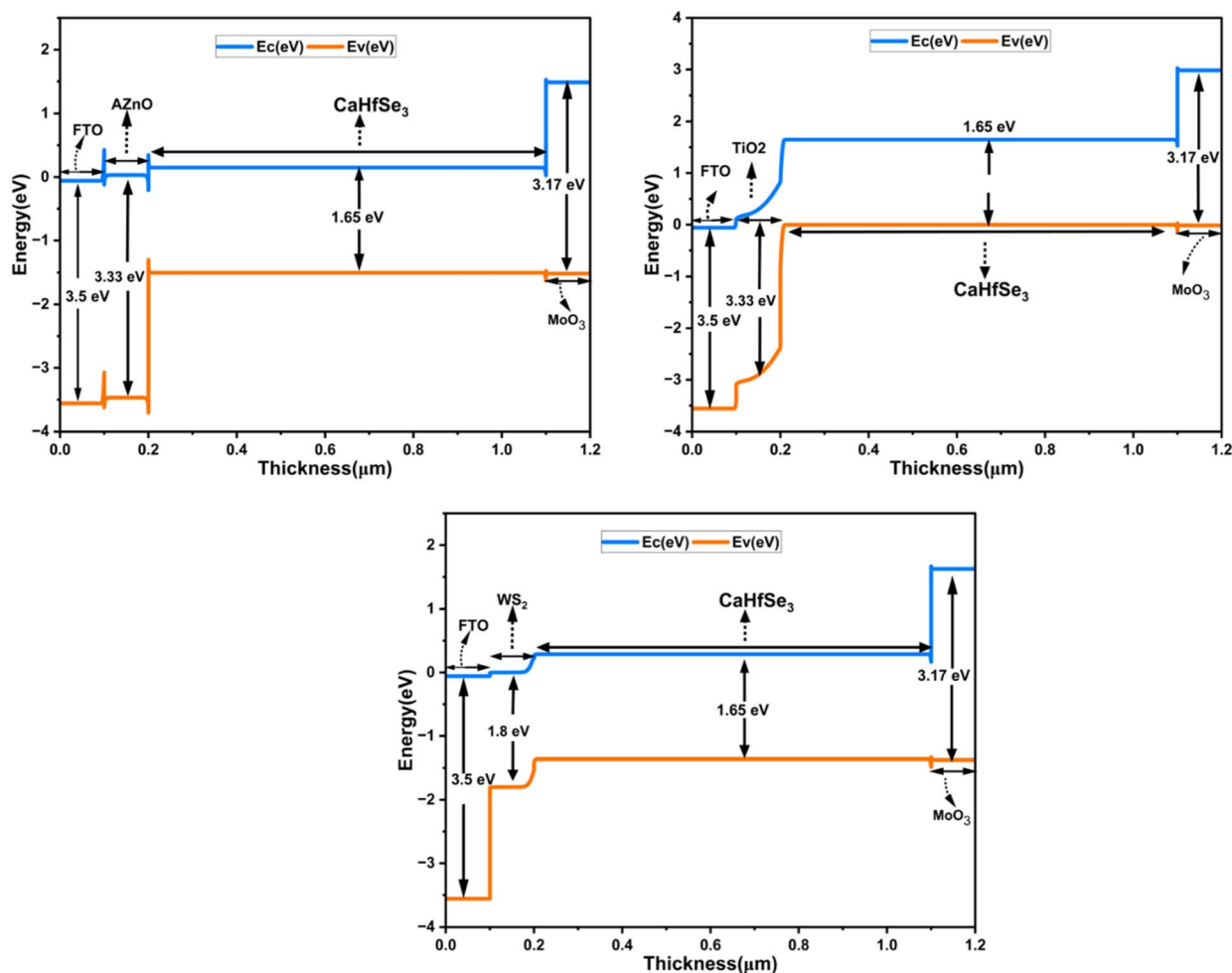


Fig. 2  $\text{CaHfSe}_3$ -based PSC energy diagram with  $\text{MoO}_3$  as the HTL and (a)  $\text{AZnO}$ , (b)  $\text{TiO}_2$ , and (c)  $\text{WS}_2$  as the ETL.



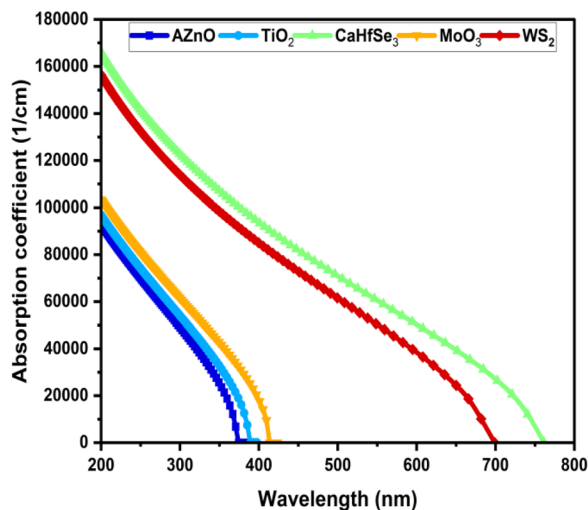


Fig. 3 Absorption coefficients of CaHfSe<sub>3</sub>, TiO<sub>2</sub>, AZnO, WS<sub>2</sub>, and MoO<sub>3</sub> as a function of wavelength.

throughout the device's many layers. This knowledge facilitates the analysis of charge carrier dynamics, which involves the movement and recombination of electrons and holes to generate energy. The continuity equations reflect the principle of charge conservation and describe the motion of charge carriers in semiconductors. In this case, eqn (2) and (3) represent continuity equations for electrons and holes, respectively.

$$\frac{dp}{dt} = \frac{1}{q} \frac{dJ_p}{dx} + R_p(x) - G(x) \quad (2)$$

$$\frac{dn}{dt} = \frac{1}{q} \frac{dJ_n}{dx} + R_n(x) - G(x) \quad (3)$$

where  $G$  is the photogeneration rate,  $R_n$  and  $R_p$  are the rates of recombination of electrons and holes, respectively and  $J_n$  and  $J_p$  being the electrical current densities of electrons and holes. In semiconductor materials, electrons or holes can be migrating for two reasons—there is an electric field that produces a drift

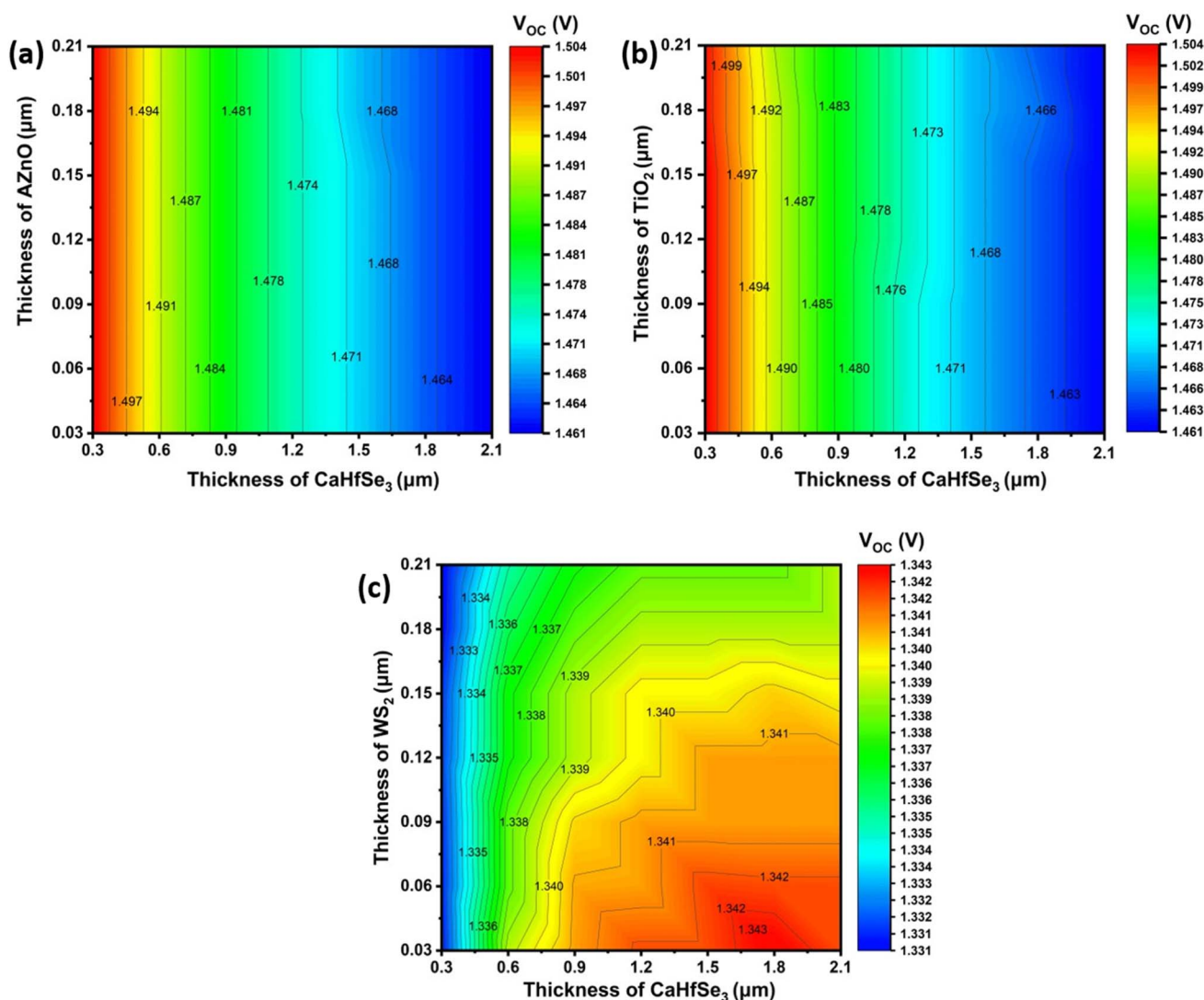


Fig. 4  $V_{OC}$  contour mapping for (a) AZnO, (b) TiO<sub>2</sub>, and (c) WS<sub>2</sub> ETLs with CaHfSe<sub>3</sub> absorber thickness.





current or there is a concentration gradient of carriers so that there is a diffusion current. Eqn (4) and (5) describe the electrical current densities associated with electron and hole transport.

$$J_n(x) = qD_n \frac{\partial n}{\partial x} + q\mu_n(n) \frac{\partial \phi}{\partial x} \quad (4)$$

$$J_p(x) = qD_p \frac{\partial p}{\partial x} + q\mu_p(p) \frac{\partial \phi}{\partial x} \quad (5)$$

Using the optical absorption model, the optical absorption constant  $\alpha$  is computed, as shown in eqn (6).

$$\alpha(\lambda) = \left( A + \frac{B}{h\nu} \right) \sqrt{h\nu - E_g} \quad (6)$$

where  $\nu$  is the radiation frequency,  $E_g$  is the material's real band gap,  $h$  is Planck's constant, and  $A$  and  $B$  are the model parameters.

## 2.2. Simulation settings and device structure

In the current work, SCAPS-1D Software was used to model a device with the structure of (back metals/MoO<sub>3</sub>/CaHfSe<sub>3</sub>/ETMs/FTO), as shown generally in Fig. 1, to simulate the one-dimensional performance of a thin films photovoltaic device. The ETMs WS<sub>2</sub>, AZnO, and TiO<sub>2</sub> were used due to their properties that complement the structural and electronic fabric of the ETLs for improved extraction of electrons through the layers to the collecting circuits of solar cell architectures. The two different ETLs are used along with MoO<sub>3</sub> as a hole transport layer or HTL layer and the studies explored the pairs of combinations that produced the best configuration for the device. The materials used for the CaHfSe<sub>3</sub> absorber layer, the FTO-coated glasses, which are transparent conducting materials, and the back contact varied with Cu, Fe, Au, C, Ni, and Pt. The project is focused on improving the metrics and performance of CaHfSe<sub>3</sub>-based lead-free perovskite solar cells by simulating modifications to the HTLs (WS<sub>2</sub>, AZnO, TiO<sub>2</sub>), and ETL(MoO<sub>3</sub>), and the back contacts (Cu, Fe, Au, C, Ni, Pt). For

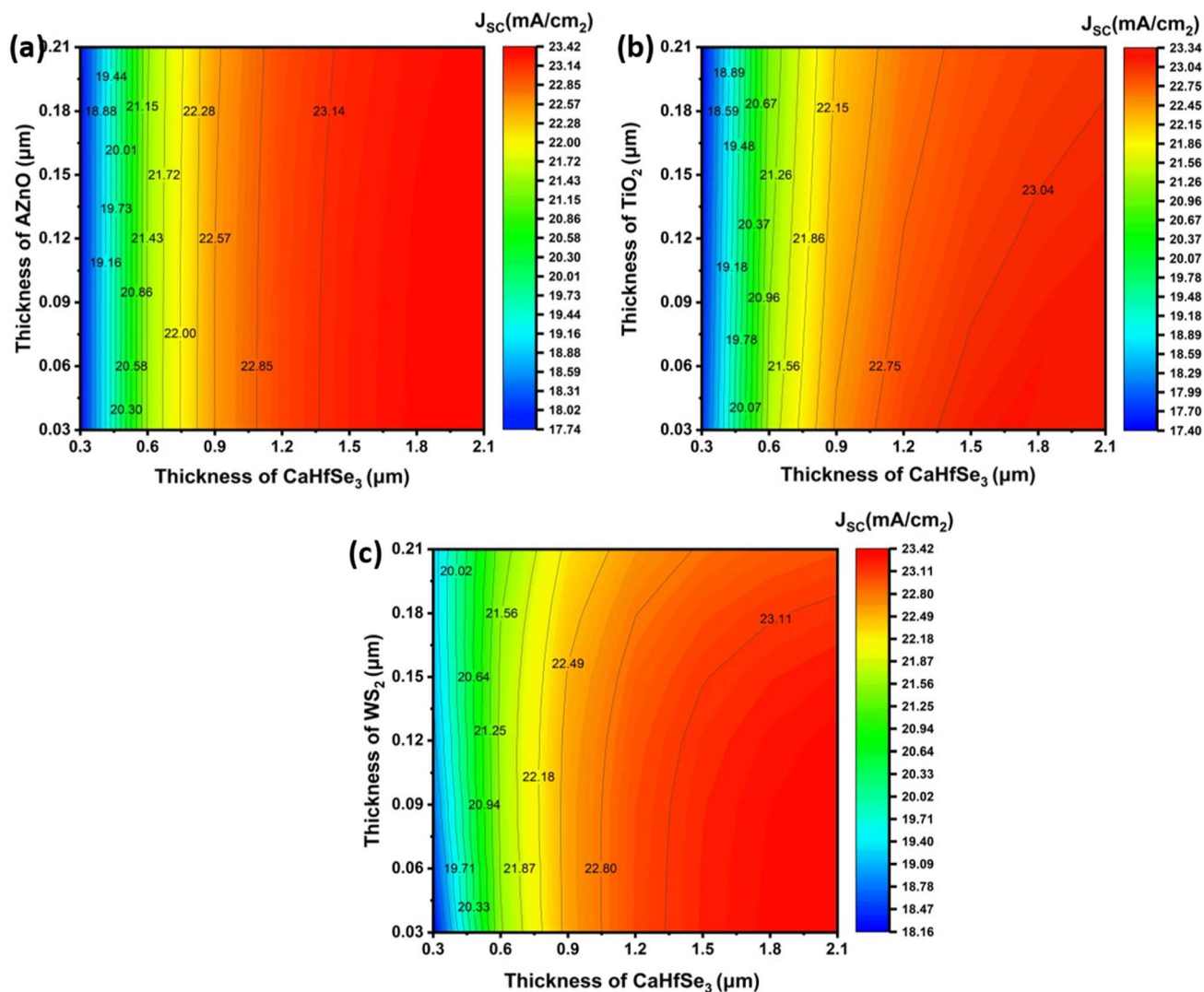


Fig. 5  $J_{sc}$  contour mapping for (a) AZnO, (b) TiO<sub>2</sub>, and (c) WS<sub>2</sub> electron transport layers (ETLs) as a function of CaHfSe<sub>3</sub> absorber thickness.



each layer, key parameters were defined, such as thickness, bandgap energy, electron affinity, permittivity, doping concentration, carrier mobilities, and defect densities, are listed in Table 1.

Table 2 presents the work functions of various materials, including Gold (Au), Nickel (Ni), Carbon (C), Iron (Fe), Copper (Cu), and Platinum (Pt). The simulations were conducted under standard AM1.5G illumination ( $1000 \text{ W m}^{-2}$ ) at an operating temperature of 300 K. Additionally, series/shunt resistances and working temperature were incorporated to reflect realistic electrical behavior. Device performance was assessed using  $J$ - $V$  characteristics, quantum efficiency (QE), and power conversion efficiency (PCE), with systematic variation of key parameters to determine the optimal configuration.

### 3. Outcome analysis and interpretation

#### 3.1. The band diagram of the model cell

Simulated band diagrams for the proposed structures are shown in Fig. 2, highlighting the importance of energy level

alignment in achieving efficient charge separation and high photovoltaic performance. To ensure effective electron transport, the electron affinity of the electron transport layer (ETLs) must exceed that of the  $\text{CaHfSe}_3$  absorber, facilitating downward conduction band alignment.<sup>22</sup> Conversely, hole extraction is enhanced when the ionization potential of the hole transport layer ( $\text{MoO}_3$ ) is lower than that of the absorber, ensuring a smooth flow of holes.<sup>23</sup>

The  $\text{WS}_2/\text{CaHfSe}_3$  interface exhibits a small CBO (0.02 eV), indicating good energy level continuity and promoting efficient electron transport. In the case of  $\text{TiO}_2$ , which has a wide  $E_g$  of 3.33 eV, the conduction band alignment (0.01 eV) also supports efficient electron extraction while acting as a barrier to hole backflow. The  $\text{AZnO}/\text{CaHfSe}_3$  interface shows a conduction band offset of approximately 0.03 eV, reflecting strong energetic compatibility and potential for high electron collection efficiency. On the hole transport side, the  $\text{CaHfSe}_3/\text{MoO}_3$  interface demonstrates a favorable valence band offset (VBO), as the valence band maximum (VBM) of  $\text{MoO}_3$  lies below that of  $\text{CaHfSe}_3$ . This ensures selective and efficient hole extraction while suppressing electron recombination at the back contact.

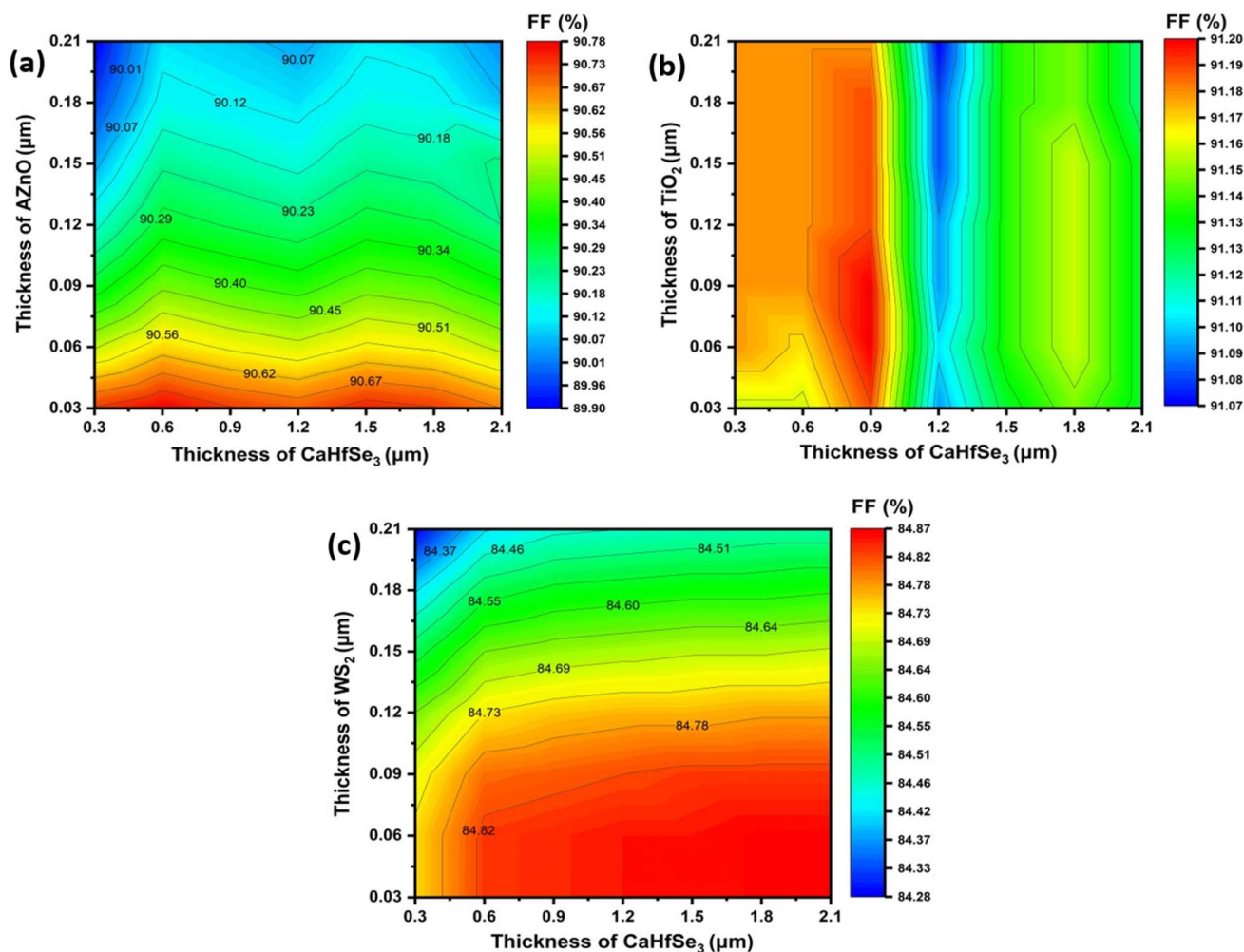


Fig. 6 Contour mapping of the fill factor (FF %) for different ETL materials: (a) AZnO, (b)  $\text{TiO}_2$ , and (c)  $\text{WS}_2$ .



Altogether, these band alignments confirm the suitability of  $\text{WS}_2$ ,  $\text{TiO}_2$ , and  $\text{AZnO}$  as ETLs, and  $\text{MoO}_3$  as an HTL, in facilitating efficient charge separation and transport in  $\text{CaHfSe}_3$ -based photovoltaic devices.

### 3.2. Coefficient of absorption

The coefficient of absorption ( $\alpha$ ) as a function of wavelength indicates a material's ability to absorb light across various regions of the electromagnetic spectrum (UV, visible, and infrared). Fig. 3 displays the theoretical absorption profiles for all layers. The absorbent material  $\text{CaHfSe}_3$  is notable for its strong Capability of absorbing radiation in the visible region, with values exceeding  $10^5 \text{ cm}^{-1}$  between 400 and 770 nm. This characteristic makes it an excellent choice for harnessing solar light and producing charge carriers.  $\text{TiO}_2$  and  $\text{AZnO}$ , used as electron transport layers (ETL), exhibit very low absorption coefficients (less than  $10^2 \text{ cm}^{-1}$  between 350 nm and 700 nm), allowing light to pass through with minimal absorption and facilitating optimal transmission to the active  $\text{CaHfSe}_3$  layer. Finally,  $\text{MoO}_3$ , used as a hole transport layer (HTL),

demonstrates intermediate behavior with a low absorption coefficient (around  $10^3$ ) in the 350–700 nm range, minimizing interaction with incident light. Its absorption increases slightly in the UV range but remains compatible with its role.<sup>24</sup>

### 3.3. Impact of ETL and absorber thickness on device performance

To improve light harvesting and promote efficient extraction of charge carriers, the absorption and ETL thicknesses must be carefully chosen and optimized. Maximum photon absorption in the active layer and efficient electron transport are ensured by a well-optimized design. In this study, contour plots were used to investigate the impact of absorber and ETL thickness variations on the performance of  $\text{CaHfSe}_3$  architectural performance has been investigated. Through this research, we can investigate how altering the thickness of the absorber and electron transport layers affects key performance metrics, including  $V_{\text{OC}}$ , FF,  $J_{\text{SC}}$ , and PCE. To identify the optimal thickness combinations for enhanced device performance, the contour plots display the predicted values of  $J_{\text{SC}}$ ,  $V_{\text{OC}}$ , FF, and PCE across

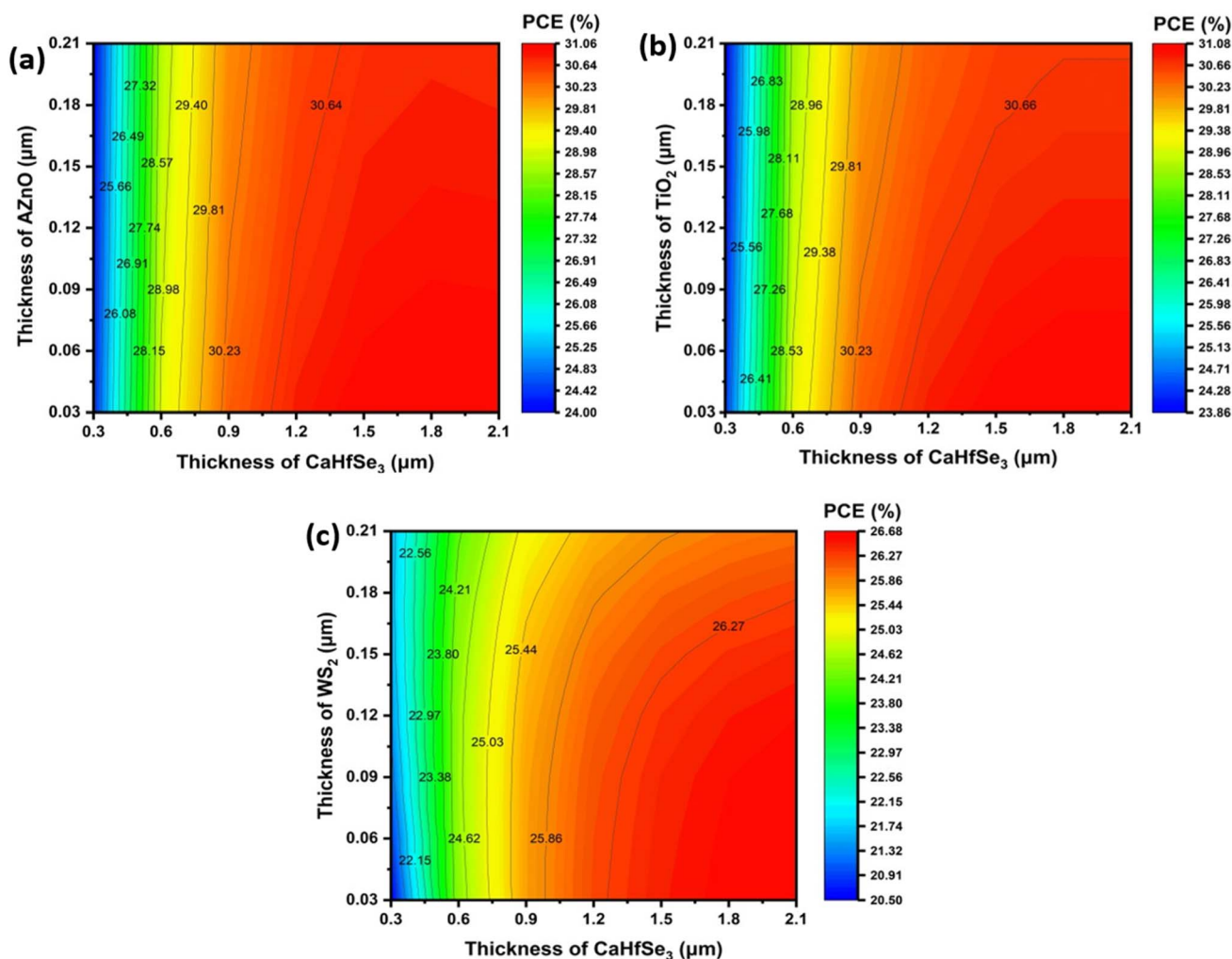


Fig. 7 Contour mapping of PCE (%) when ETL is (a)  $\text{AZnO}$ , (b)  $\text{TiO}_2$ , and (c)  $\text{WS}_2$ .



a range of absorber thicknesses (300 to 2100 nm) and ETL thicknesses (from 30 to 210 nm). In this investigation section,  $\text{MoO}_3$  was held constant as the HTM. Fig. 4 shows the impact of absorber layer thickness and ETL on the  $V_{\text{OC}}$ . Under conditions where the absorber and ETL layers were about 300 nm and <150 nm in thickness, respectively, the perovskite employing  $\text{TiO}_2$  and  $\text{AZnO}$  as ETLs reached a peak  $V_{\text{OC}}$  of 1.54 V, as illustrated in Fig. 4(a and b). As the thicknesses of both the absorber and ETL layers grew, the open-circuit voltage ( $V_{\text{OC}}$ ) exhibited a decline. This decrease can be attributed to a rise in the reverse saturation current caused by the thicker absorber, combined with the partial absorption of incident light within the thicker ETL layers. By contrast, when absorber and ETL thicknesses were approximately 1500 nm and  $\leq 30$  nm, respectively, the PSC with a  $\text{WS}_2$  ETL showed a maximum  $V_{\text{OC}}$  of 1.34 V.

The influence of changes in the absorber layer thickness and ETL on the  $J_{\text{SC}}$  parameter of three selected perovskite solar cells is illustrated in Fig. 5. The PSC incorporating  $\text{TiO}_2$  as the ETL achieved a maximum current density of  $23.33 \text{ mA cm}^{-2}$  once the absorber layer exceeded 1800 nm and the ETL thickness was

$\geq 30$  nm. Under conditions where the absorber measured 2100 nm and the thickness of ETL ranged from 30 to 210 nm, the ETL  $\text{AZnO}$  demonstrated the greatest  $J_{\text{SC}}$  of  $23.4 \text{ mA cm}^{-2}$ . In addition, the PSCs using  $\text{WS}_2$  ETL exhibited maximum ( $J_{\text{SC}}$ ) of  $23.4 \text{ mA cm}^{-2}$  when the absorber thickness was 2100 nm and the ETL thickness ranged from 30 to 90 nm. Generally, an increase in absorber thickness led to higher  $J_{\text{SC}}$  values in each device, as a thicker absorber enhances photon absorption, promotes greater electron-hole pair generation, and consequently boosts the photocurrent. This enhancement is also ascribed to the improved spectral responsiveness at extended wavelengths. Fig. 6 illustrates how different absorber and ETL layer thicknesses affect FF values. When  $\text{WS}_2$  is implemented as the electron transport layer (ETL) in solar cell structures, studies have revealed that the FF of  $\text{BaHfSe}_3$ -based solar cells increase with absorber thickness up to 1.8–2.1  $\mu\text{m}$ , while it slightly decreases as the  $\text{WS}_2$  layer becomes thicker. The highest FF value of 84.86% is recorded when the  $\text{BaHfSe}_3$  thickness ranges from 1.8 to 2.1  $\mu\text{m}$  and the  $\text{WS}_2$  thickness is between 0.03 and 0.06  $\mu\text{m}$ , Fig. 6(b).

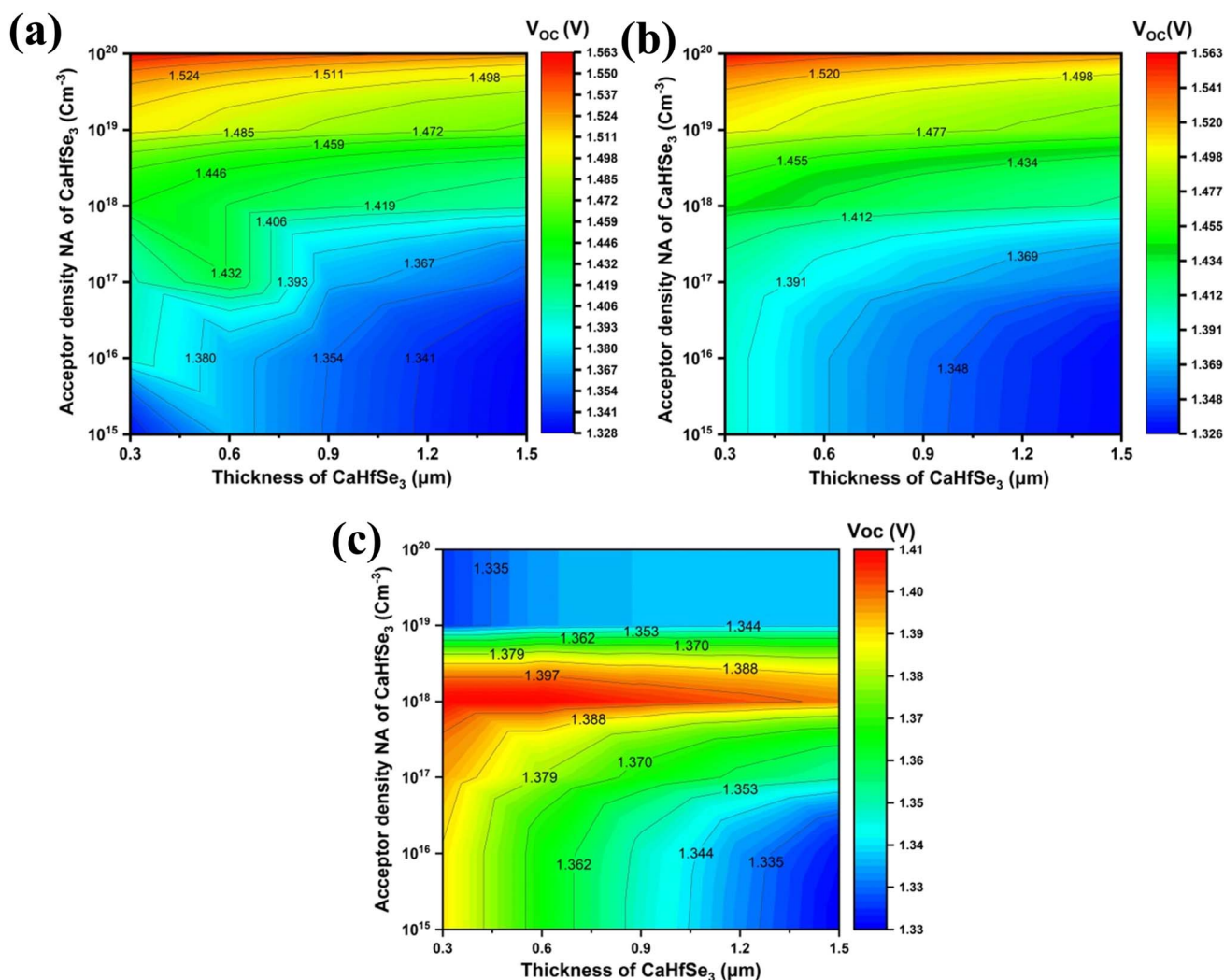


Fig. 8 Contour plots illustrate the influence of absorber doping concentration and thickness on  $V_{\text{OC}}$  for ETL types (a)  $\text{AZnO}$ , (b)  $\text{TiO}_2$ , and (c)  $\text{WS}_2$ .





Using  $\text{TiO}_2$  as an ETL results in a maximum fill factor (FF) of 91.2% with a  $\text{BaHfSe}_3$  thickness of 0.9  $\mu\text{m}$  and a  $\text{TiO}_2$  layer thickness ranging from 0.06 to 0.09  $\mu\text{m}$ . In contrast, increasing the thickness of  $\text{BaHfSe}_3$  beyond 1.2  $\mu\text{m}$  leads to a slight decline in FF, likely resulting from enhanced recombination losses or reduced efficiency in charge transport. Furthermore, Fig. 6(a) illustrates that the  $\text{AZnO}$  electron transport layer thickness significantly impacts the fill factor (FF), with ultrathin layers ( $\leq 0.03$   $\mu\text{m}$ ) showing optimal values ( $\sim 90.7\%$ ). FF gradually decreases as  $\text{AZnO}$  thickness increases, primarily due to heightened recombination losses and series resistance. Conversely, variations in the  $\text{BaHfSe}_3$  absorber's thickness have minimal effect on the FF, indicating consistent device performance over a wide thickness range (0.3–2.1  $\mu\text{m}$ ), as charge carrier extraction and production remain unchanged. Fig. 7 displays the simulation findings showing distinct performance characteristics for the three ETLs when incorporated into  $\text{BaHfSe}_3$ -based solar cells.  $\text{AZnO}$ -based devices reach a top PCE of 31.05% when configured with a 1.8  $\mu\text{m}$  absorber and a 30 nm ETL, showcasing a favorable trade-off between efficiency and material economy. Notably,  $\text{AZnO}$  maintains good efficiency at

reduced absorber thicknesses, making it a low-cost and easy-to-fabricate alternative. However, the devices with  $\text{TiO}_2$  exhibit competitive performance, achieving a slightly higher maximum PCE of 31.08% with a thicker absorber layer of 2.1  $\mu\text{m}$ . Its reliance on increased thickness implies a greater dependence on photon absorption to compensate for its reduced electron mobility. Conversely,  $\text{WS}_2$  shows a lower overall efficiency, with a maximum PCE of 26.67% occurring at  $\text{WS}_2$  thicknesses less than 0.15  $\mu\text{m}$  combined with absorber thicknesses ranging from 1.8 to 2.1  $\mu\text{m}$ .

There are several reasons for the noticeable differences in  $V_{\text{OC}}$ ,  $J_{\text{SC}}$ , FF, and PCE across perovskite with various ETL. The absorption coefficient is a crucial component that greatly impacts photovoltaic metrics, including  $V_{\text{OC}}$ ,  $J_{\text{SC}}$ , FF, and PCE. This parameter affects the coupling efficiency of light photons with the underlying  $\text{CaHfSe}_3$  absorber layer and is directly correlated with the ETL's bandgap. The overall efficiency of the solar cell is significantly affected by the CBO, arising from the disparity in electron affinity and Fermi level positions between the absorber and the ETL.

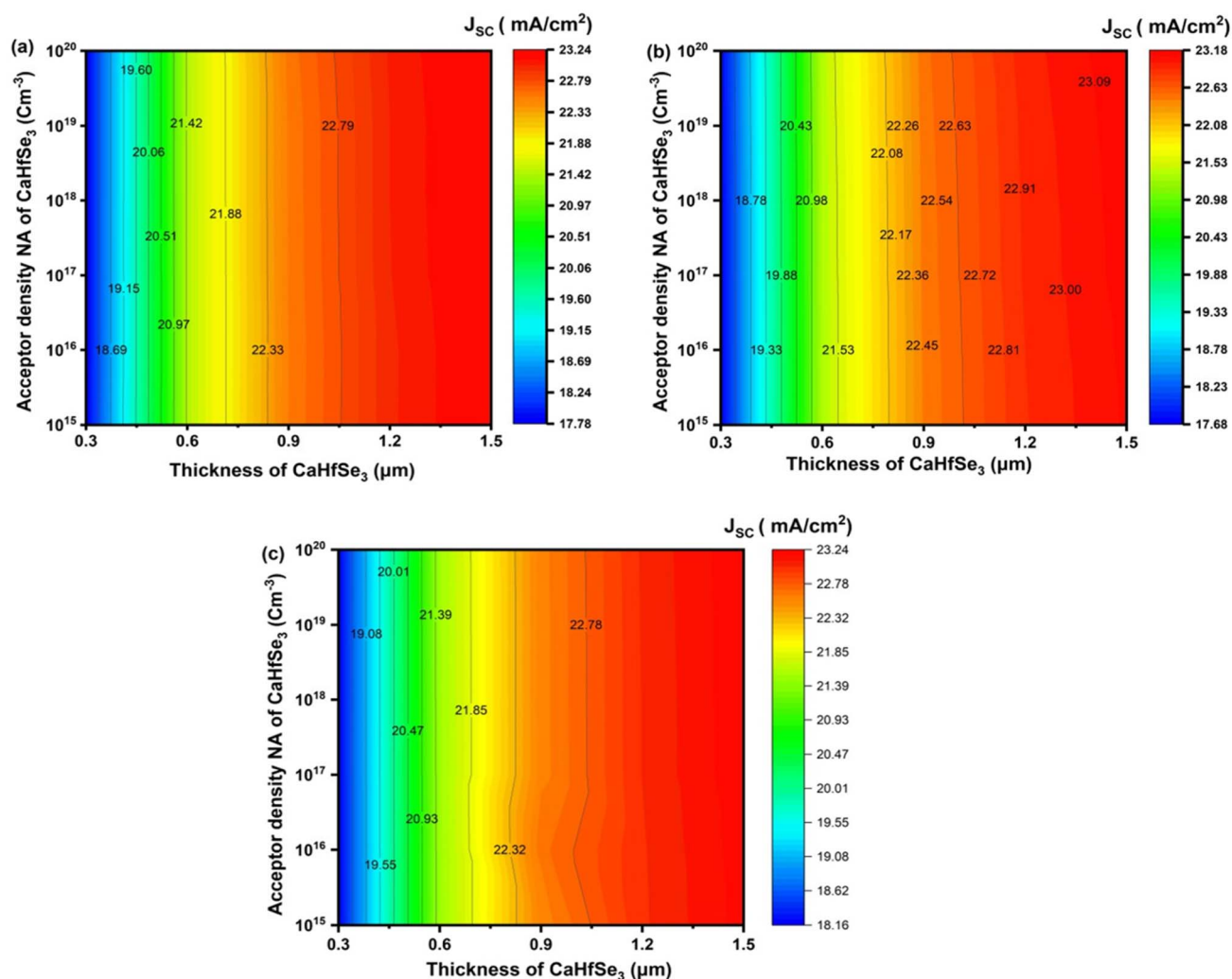


Fig. 9 Contour plots illustrate the influence of absorber doping concentration and thickness on  $J_{\text{SC}}$  for ETL types (a)  $\text{AZnO}$ , (b)  $\text{TiO}_2$ , and (c)  $\text{WS}_2$ .



### 3.4. Effect of absorber acceptor concentration and layer thickness on photovoltaic performance

Optimizing both the absorber thickness and  $N_A$  within the absorber is essential for achieving improved efficiency. To examine the impact of these factors, we conducted simulations by adjusting the acceptor doping density ( $N_A$ ) from  $1 \times 10^{15}$  to  $1 \times 10^{20} \text{ cm}^{-3}$  and absorber thickness from 0.3 to 1.5  $\mu\text{m}$  across seven distinct PSC configurations. Fig. 8 shows how variations in absorber thickness and  $N_A$  influence the ( $V_{OC}$ ) in the validated PSC configurations.

According to Fig. 8, under conditions where the absorber was less than 0.9  $\mu\text{m}$  thick and the acceptor doping concentration ( $N_A$ ) was fixed at  $10^{20} \text{ cm}^{-3}$ , AZnO and  $\text{TiO}_2$  achieved their maximum  $V_{OC}$  values of 1.5 V. Notably, increasing the absorber thickness beyond this threshold resulted in a gradual decline in  $V_{OC}$  for all ETLs under the same doping conditions. The data's shape makes it evident that while  $V_{OC}$  tends to drop with increasing absorber thickness, it increases with increased

acceptor concentration ( $N_A$ ). This behavior is explained by the stronger electric field and greater built-in potential at higher doping levels, which makes it easier to separate and remove photogenerated carriers and increase  $V_{OC}$ . Nevertheless, the series resistance rises, and the greater sheet resistance at thicker absorber layers constrains the hole mobility towards the HTL. This leads to a decrease in carrier collection and, thus, a lower  $V_{OC}$ .<sup>25</sup>

Fig. 9(a)–(c) show that the short-circuit current density  $J_{SC}$  for devices using ZnO,  $\text{TiO}_2$ , and  $\text{WS}_2$  as ETL shows a significant increase with absorber thickness and a modest increase with increasing acceptor density ( $N_A$ ). The maximum  $J_{SC}$  values of  $23.239 \text{ mA cm}^{-2}$ ,  $23.169 \text{ mA cm}^{-2}$  and  $23.232 \text{ mA cm}^{-2}$  for ZnO,  $\text{TiO}_2$ , and  $\text{WS}_2$ , respectively, were observed at an absorber thickness of 1.5  $\mu\text{m}$  with  $N_A = 10^{20} \text{ cm}^{-3}$ . The increased light absorption in the thicker  $\text{CaHfSe}_3$  absorber layer, which permits a bigger production of photogenerated carriers, is primarily responsible for the progressive increase in  $J_{SC}$  seen for all ETLs from 0.3  $\mu\text{m}$  to 1.5  $\mu\text{m}$ . Furthermore, for a constant thickness,

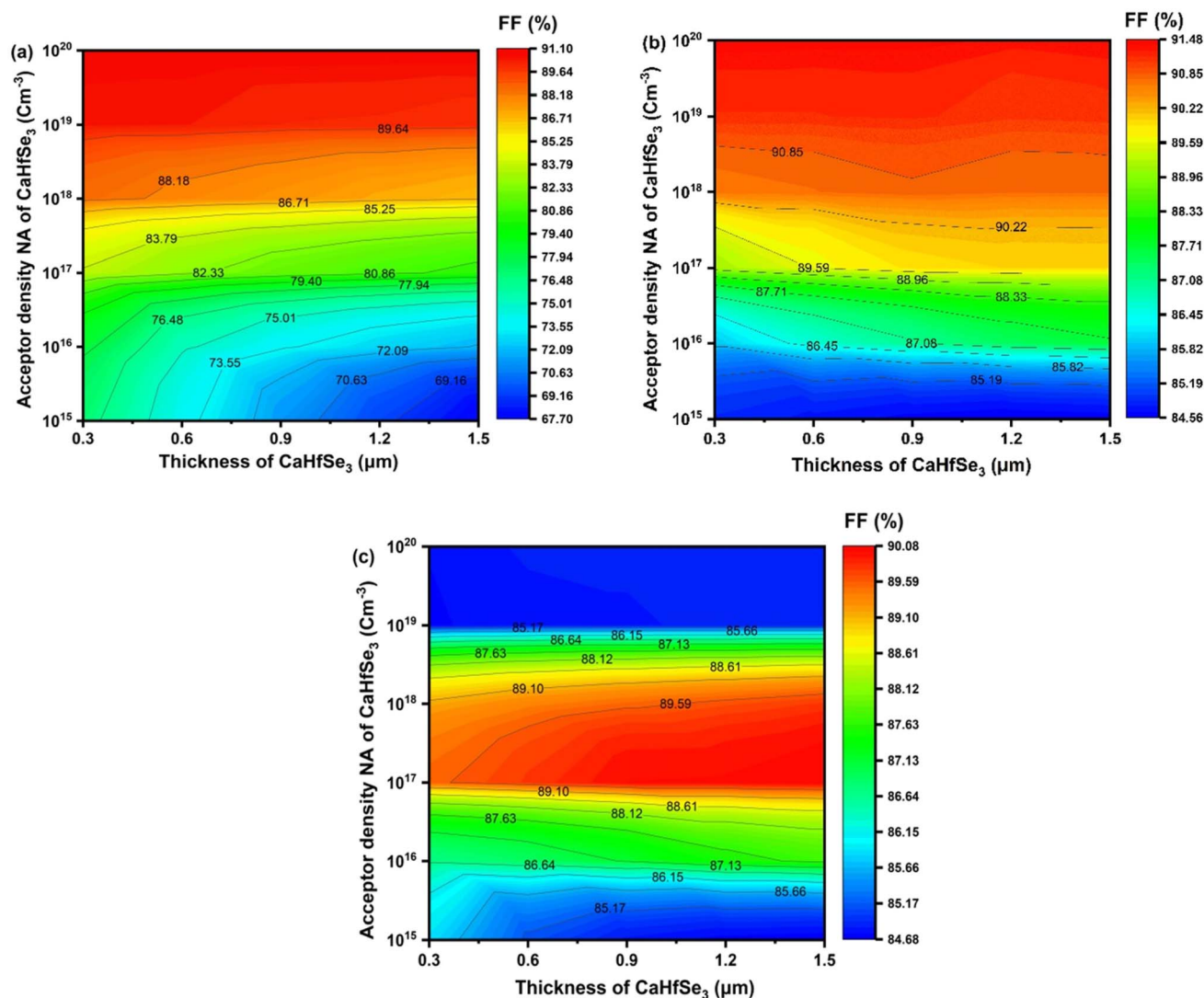


Fig. 10 Impact of (a) AZnO, (b)  $\text{TiO}_2$ , and (c)  $\text{WS}_2$  ETLs on FF (%) contour plots in  $\text{CaHfSe}_3$  perovskite solar cells.



the  $J_{SC}$  values are rather stable over  $N_A$  values and improve slightly with increasing  $N_A$ . This is explained by the improved separation of photogenerated carriers in highly doped materials, leading to more effective electric field generation and less recombination. Fig. 10(a)–(c) illustrate that, for all three ETLs, the fill factor (FF) typically increases with the rising acceptor density ( $N_A$ ) throughout all examined thicknesses.

This enhancement results from minimized carrier recombination and enhanced charge transport as a result of increased doping levels.  $TiO_2$  often demonstrates the highest fill factor values, achieving 91.48% at a minimal thickness of 0.3  $\mu m$  and elevated doping levels ( $N_A > 10^{19} cm^{-3}$ ). This exceptional performance is attributed to its effective surface passivation characteristics and favorable band alignment with  $CaHfSe_3$ , which reduces non-radiative recombination. At low acceptor densities, AZnO exhibits lower FF values than  $TiO_2$ , but, when  $N_A$  rises, it shows notable improvement, reaching up to 91.03–91.06% for  $N_A = 10^{20} cm^{-3}$ . However, we observe that the  $WS_2$ -based solar cell structure exhibits a maximum FF value,

reaching nearly 90% when the thickness of absorber exceeds 0.8  $\mu m$ , and  $N_A$  ranges from  $10^{17}$  to  $10^{18} cm^{-3}$ .

Fig. 11(a) and (b) highlight the combined effect of absorber thickness and  $N_A$  on the performance of  $CaHfSe_3$ -based solar cells. The simulations show that the PCE reaches its peak at absorber thicknesses of 1.2  $\mu m$  and 1.5  $\mu m$ , achieving 32.30% for AZnO and 32.40% for  $TiO_2$  when  $N_A$  exceeds  $10^{19} cm^{-3}$ . A reduction in absorber thickness leads to a noticeable drop in PCE, since thinner layers allow a considerable fraction of incident photons to pass through unabsorbed, thereby limiting electron–hole pair generation. Conversely, thicker absorbers enhance light absorption, increase carrier generation, and result in higher efficiencies. In addition, the PCE improves with increasing  $N_A$ , as higher acceptor doping concentrations strengthen the built-in electric field, which facilitates the separation and transport of photogenerated carriers, reduces recombination losses, and ultimately enhances device performance.<sup>26</sup> Fig. 11(c) shows that using  $WS_2$  as the ETL results in a PCE of 29.12% when the absorber thickness exceeds 1.2  $\mu m$

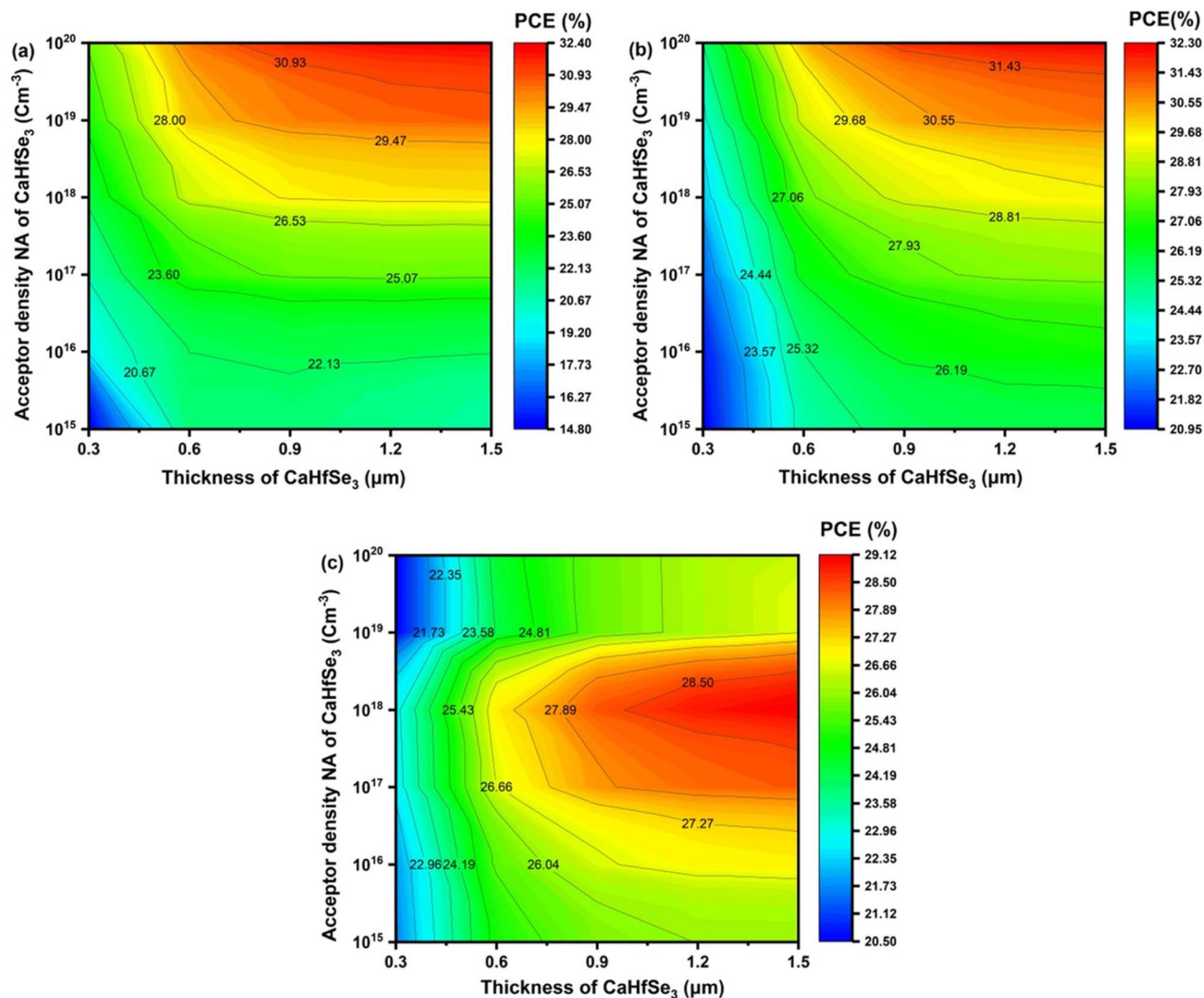


Fig. 11 PCE (%) contour plots with ETL as (a)AZnO, (b)  $TiO_2$ , and (c)  $WS_2$ .



and the  $N_A$  is approximately  $10^{18} \text{ cm}^{-3}$ . This phenomenon occurs because a high acceptor density increases the recombination rate, restricting carrier mobility and subsequently reducing the PCE.

### 3.5. Influence of defect density and $\text{CaHfSe}_3$ layer thickness on photovoltaic performance

Defect density is a crucial factor that significantly impacts perovskite solar cells (PSCs). Absorber layer defects, acting as recombination sites, reduce carrier lifetimes and decrease device efficiency. Consequently, achieving excellent performance necessitates reducing the absorber layer's defect density. Numerous studies have focused on the interplay between defect density and absorber thickness in  $\text{CaHfSe}_3$ -based PSCs and their effect on device efficiency and the results demonstrate a significant relationship between the two factors. Optimizing both simultaneously can result in the most efficient device possible.

Hence, the thickness of the  $\text{CaHfSe}_3$  absorber ranged from 300 nm to 1500 nm, alongside  $N_t$  values adjusted from  $10^{13}$  to  $10^{15} \text{ cm}^{-3}$ . The simulation outcomes indicate that both the absorber thickness and  $N_t$  substantially affect the  $V_{OC}$  of

$\text{CaHfSe}_3$ -based solar cells, as shown in Fig. 12. For all evaluated ETLs (AZnO,  $\text{TiO}_2$ , and  $\text{WS}_2$ ), in configurations (a) and (b),  $V_{OC}$  exhibits a strong dependence on both thickness and defect density. When  $N_t$  is maintained below  $10^{14} \text{ cm}^{-3}$ ,  $V_{OC}$  reaches values as high as 1.448 V, indicating minimal nonradiative recombination and efficient carrier extraction. The voltage increases with thickness up to approximately 0.9  $\mu\text{m}$ , beyond which the gain plateaus, suggesting that additional thickness does not significantly enhance photogeneration or reduce recombination. This behavior reflects a balance between optical absorption and carrier diffusion length, where excessive thickness may introduce resistive losses or trap-limited transport without further improving voltage. As  $N_t$  increases beyond  $10^{16} \text{ cm}^{-3}$ , a pronounced decline in  $V_{OC}$  is observed, regardless of thickness. This trend highlights the detrimental impact of bulk and interfacial defects, which act as recombination centers and suppress quasi-Fermi level splitting. The steep voltage gradient across the defect density axis underscores the necessity of defect passivation strategies, such as surface treatments or compositional tuning, to preserve high  $V_{OC}$  values. In contrast, configuration (c) yields significantly lower  $V_{OC}$  values, ranging from 1.128 V to 1.148 V. The voltage remains relatively insensitive to

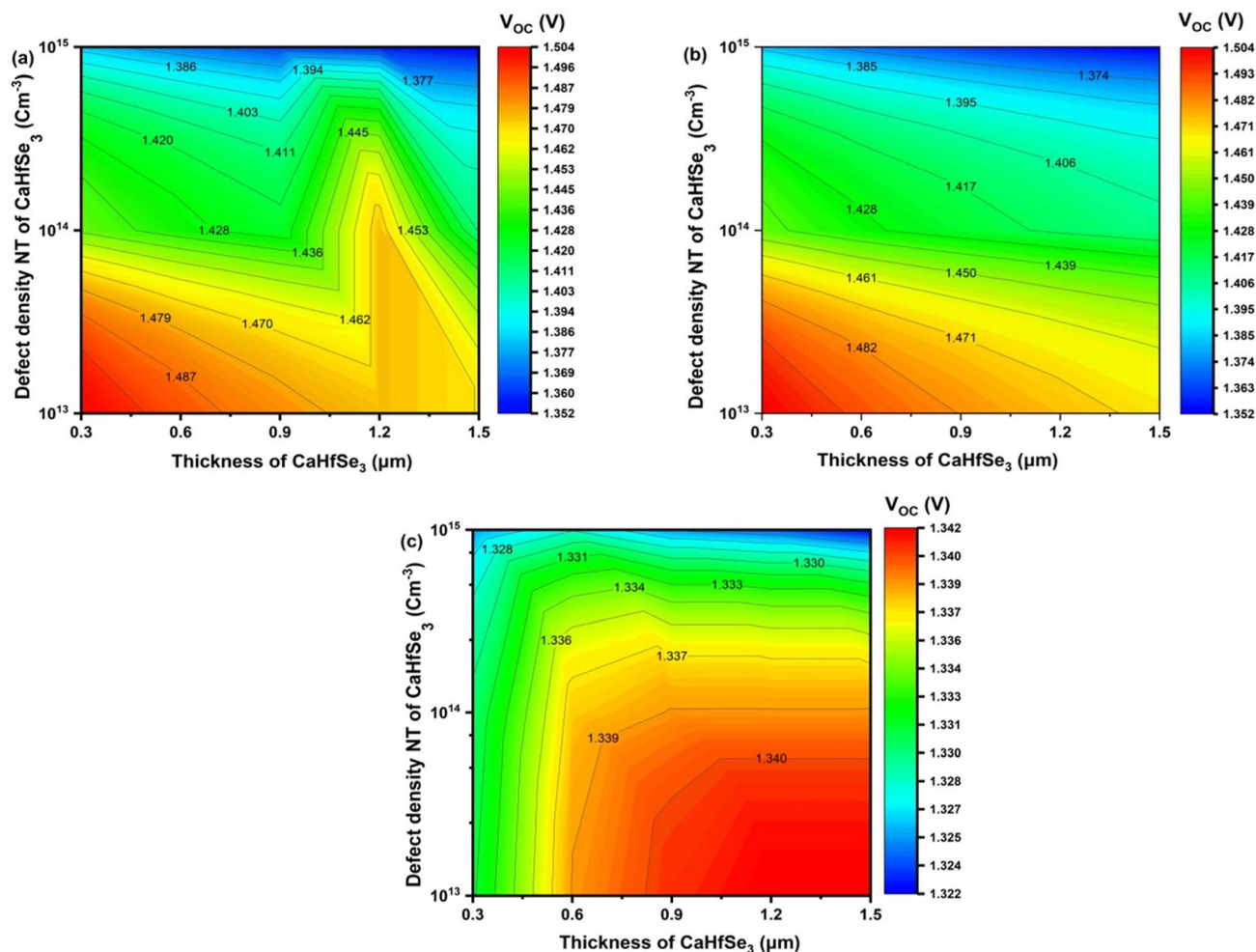


Fig. 12 Contour graphs of  $V_{OC}$  dependence on  $\text{CaHfSe}_3$  absorber thickness and defect density with ETLs as (a) AZnO, (b)  $\text{TiO}_2$ , and (c)  $\text{WS}_2$ .





thickness variations, and even at low  $N_t$ , the performance is markedly inferior to that of configurations (a) and (b). This suggests a fundamentally different device architecture or material interface, potentially characterized by poor band alignment, high interface recombination velocity, or inadequate carrier selectivity. The suppressed  $V_{OC}$  may also reflect unfavorable energetics at the contact layers or the presence of deep-level traps within the  $\text{CaHfSe}_3$  matrix. Particularly at low defect concentrations ( $N_t = 10^{13} \text{ cm}^{-3}$ ), since the longer carrier transport pathways raise the possibility of recombination. Furthermore, the greatest  $V_{OC}$  values reported are 1.504 V for both  $\text{AZnO}$  and  $\text{TiO}_2$  at  $0.3 \mu\text{m}$  thickness and  $N_t = 10^{13} \text{ cm}^{-3}$ , and 1.342 V for  $\text{WS}_2$  at  $1.2\text{--}1.5 \mu\text{m}$  thickness with the same low defect density.

Fig. 13 shows that the  $J_{SC}$  of  $\text{CaHfSe}_3$ -based solar cells is significantly influenced by both the absorber thickness and  $N_t$ . Because larger layers generate more carriers and absorb more photons,  $J_{SC}$  grows continuously with absorber thickness. Beyond  $1.2 \mu\text{m}$ , this gain tends to saturate, suggesting an ideal thickness range for balancing recombination and absorption losses. On the other hand,  $J_{SC}$  slightly decreases when the defect

density is increased from  $10^{13}$  to  $10^{15} \text{ cm}^{-3}$  at a given thickness. This is because greater trap-assisted recombination lowers the carrier collection efficiency. The maximum  $J_{SC}$  values recorded are 23.24, 23.02, and 23.24  $\text{mA cm}^{-2}$  for  $\text{AZnO}$ ,  $\text{TiO}_2$ , and  $\text{WS}_2$ , respectively. These values all correspond to a low defect density  $<10^{14} \text{ cm}^{-3}$  and an absorber thickness greater than  $1.2 \mu\text{m}$ . These results validate that adequate absorber thickness and defect passivation are both necessary to maximize photo-generated current.

For the device utilizing  $\text{AZnO}$  as the electron transport layer, Fig. 14(a), the fill factor exhibited considerable stability across varying absorber thicknesses and defect concentrations. In particular, FF values were higher than 90.50% for thicknesses  $<900 \text{ nm}$  and  $N_t < 10^{15} \text{ cm}^{-3}$ . The highest FF of 90.78% was observed at  $N_t = 10^{13} \text{ cm}^{-3}$  and thickness  $\sim 0.6 \mu\text{m}$ . At  $1.2 \mu\text{m}$  thickness, FF decreased from 90.78% to 89.76% as  $N_t$  grew from  $10^{13}$  to  $10^{15} \text{ cm}^{-3}$ , indicating a modest drop with rising  $N_t$ . Due to accumulated recombination. Thus, low  $N_t$  and thickness allow for better fill factor, especially internal losses. Furthermore, the  $\text{TiO}_2$ -based ETL device exhibited steady performance over diverse absorber thickness and  $N_t$  conditions, as presented

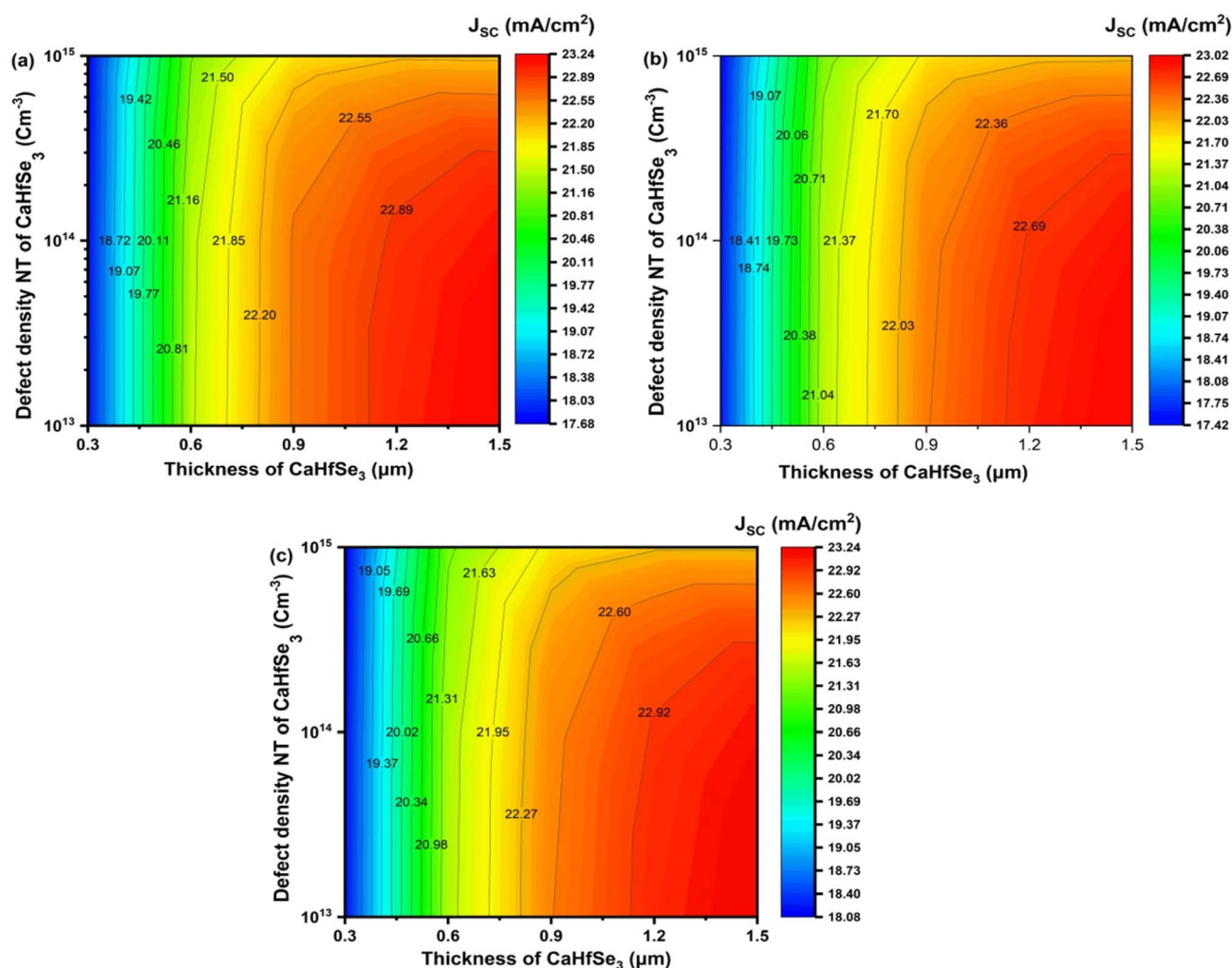


Fig. 13 Contour graphs of  $J_{SC}$  as a function of  $\text{CaHfSe}_3$  absorber thickness and defect density with ETL as (a)  $\text{AZnO}$ , (b)  $\text{TiO}_2$ , and (c)  $\text{WS}_2$ .

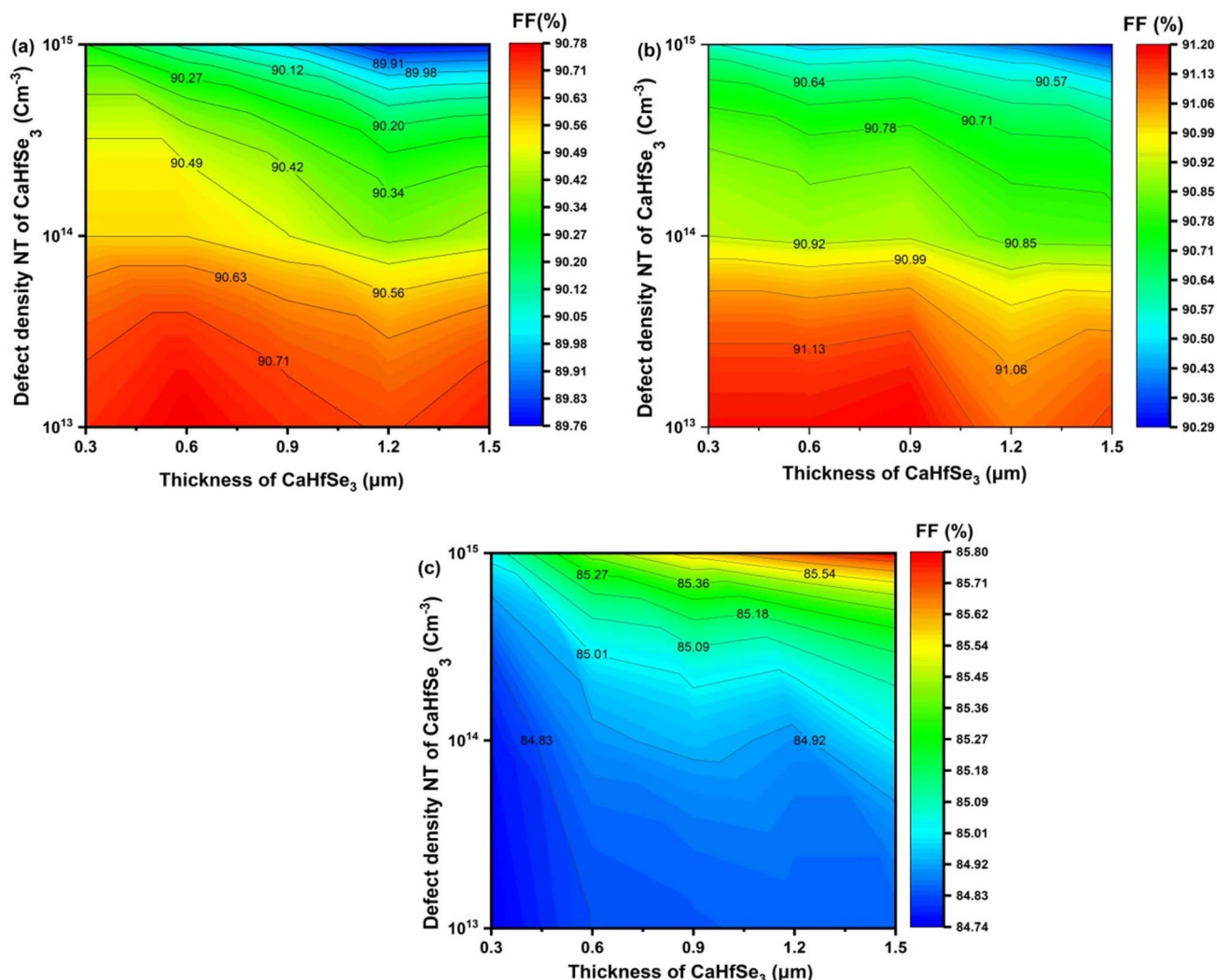


Fig. 14 Contour graphs of FF as a function of CaHfSe<sub>3</sub> absorber thickness and defect density with ETL as (a) AZnO, (b) TiO<sub>2</sub>, and (c) WS<sub>2</sub>.

in Fig. 14(b). A maximum fill factor (FF) of 91.20% was achieved at  $N_t = 1.0 \times 10^{13} \text{ cm}^{-3}$  and a thickness of 0.9  $\mu\text{m}$ . As the defect density increased, the FF gradually declined; however, it remained above 90% under all tested conditions. This highlights the excellent compatibility of TiO<sub>2</sub> with the CaHfSe<sub>3</sub> absorber layer, as well as its effectiveness in minimizing series resistance and enabling efficient charge extraction.

In contrast, the device employing WS<sub>2</sub> as the ETL displayed a lower but increasing FF trend with absorber thickness. Fig. 14(c) indicates that FF rose from 85.04% to 85.80% as thickness increased from 0.3  $\mu\text{m}$  to 1.5  $\mu\text{m}$  at  $N_t = 1.0 \times 10^{15} \text{ cm}^{-3}$ , achieving a maximum FF of 85.80%. At low  $N_t$  values ( $<10^{14} \text{ cm}^{-3}$ ), FF stayed below 85.00%, suggesting that WS<sub>2</sub> is more suitable for thicker absorbers with higher defect tolerance. The lowest result, 84.74%, was recorded at 0.3  $\mu\text{m}$  and  $N_t = 1.0 \times 10^{13} \text{ cm}^{-3}$ .

Fig. 15 shows the PCE of CaHfSe<sub>3</sub>-based solar cells utilizing three different ETLs: AZnO, TiO<sub>2</sub>, and WS<sub>2</sub>, with various absorber thicknesses and defect densities. For all ETLs, the PCE increased with absorber thickness and dropped with increasing

defect density ( $N_t$ ), which corresponded to improved light absorption and lower carrier recombination at low  $N_t$ . The device achieved a maximum PCE of 31.00% when AZnO served as the ETL, combined with a carrier concentration of  $10^{13} \text{ cm}^{-3}$  and an absorber thickness of 1.5  $\mu\text{m}$ . Moreover, Fig. 15(b) shows that the device using TiO<sub>2</sub> as the ETL demonstrated high performance, achieving a maximum PCE of 30.81% under similar conditions. In contrast, Fig. 15(c) reveals that WS<sub>2</sub> exhibited a lower peak efficiency of 26.46% at  $N_t$  equals  $1.0 \times 10^{13} \text{ cm}^{-3}$  and an absorber thickness of 1.5  $\mu\text{m}$ . While both AZnO and TiO<sub>2</sub> showed high and comparable efficiencies across all examined conditions, WS<sub>2</sub> consistently delivered lower efficiencies, particularly at low thicknesses and high defect densities. This behavior may be attributed to increased interfacial recombination or higher series resistance. These findings underscore the excellent performance and compatibility of AZnO and TiO<sub>2</sub> as ETLs for CaHfSe<sub>3</sub>-based devices, particularly when combined with low defect densities and optimized absorber thickness.



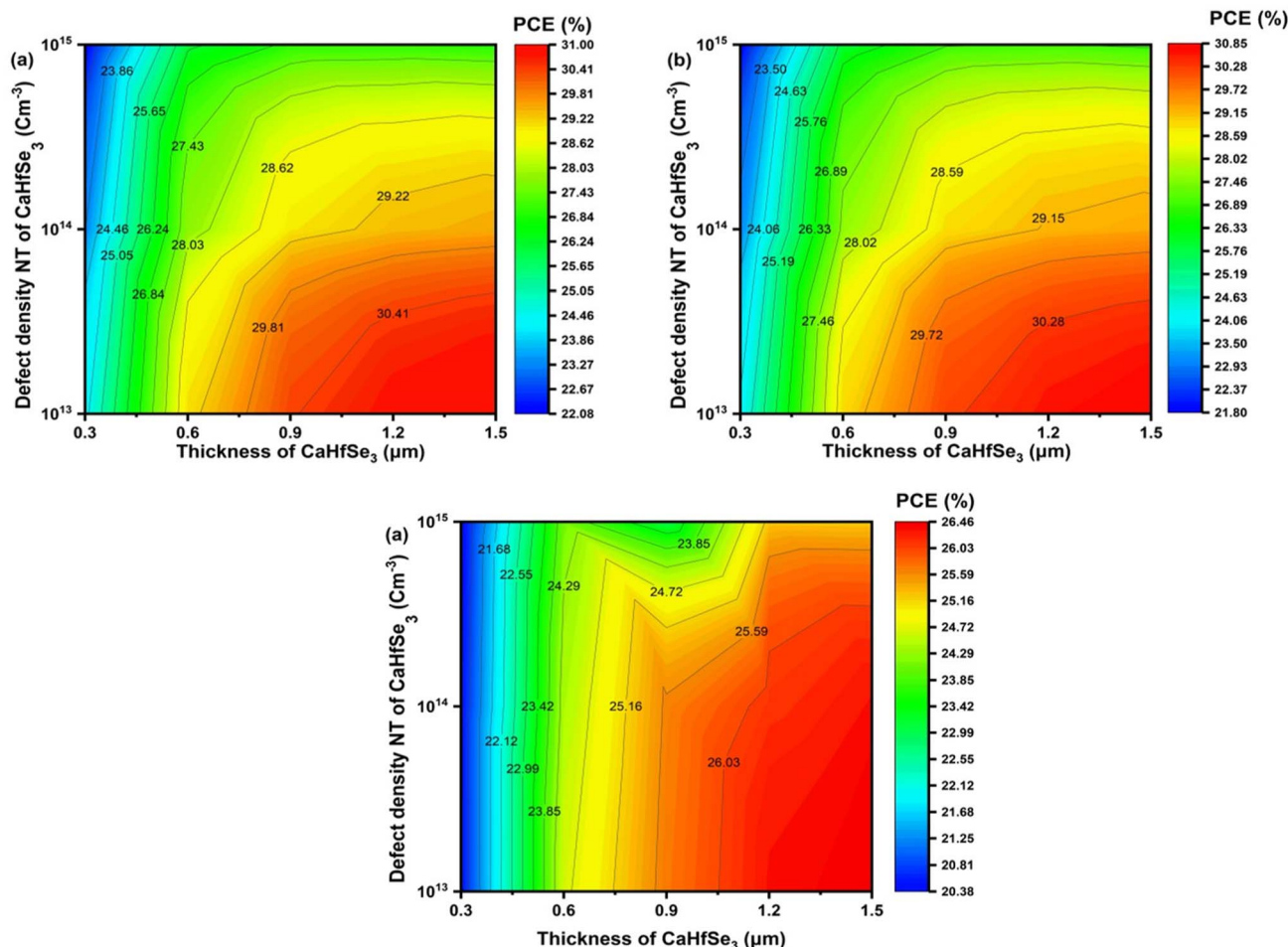


Fig. 15 PCE contour maps showing the influence of  $\text{CaHfSe}_3$  absorber thickness and defect density for ETLs including (a)  $\text{AZnO}$ , (b)  $\text{TiO}_2$ , and (c)  $\text{WS}_2$ .

### 3.6. Effect of HTM and ETM thickness and carrier concentration on PV properties

**3.6.1. Effect of HTM thickness.** The HTL improves efficiency by collecting holes, restricting electron movement, and shielding the perovskite from environmental variables including moisture, heat, and oxygen.<sup>27</sup> This section uses  $\text{AZnO}$  as the ETM and  $\text{MoO}_3$  as the HTM. HTL thickness was varied from 20–180 nm to evaluate how thickness influences the performance of a  $\text{CaHfSe}_3$ -based PSC. Fig. 16 shows that all the significant metrics for performance, namely  $V_{\text{OC}}$ ,  $J_{\text{SC}}$ , FF and PCE, were not significantly affected over the range of thicknesses and showed only slight differences in overall performance. Specifically,  $V_{\text{OC}} = 1.482 \text{ V}$ ,  $J_{\text{SC}} = 22.575 \text{ mA cm}^{-2}$ , FF = 90.73% and PCE = 30.37%. Overall, the  $\text{MoO}_3$  layer provided a suitable energy level for hole transport and sufficient holes across the range of HTL thickness without adding series resistance, or introducing any optical losses. Even the lowest thickness was suitable in ensuring effective hole extraction and hole transport (30 nm), as evidenced from the data showing that the performance metrics were not generally influenced by HTL thickness. Therefore, reduced HTL thickness is a solution to cut

material usage or production cost while remaining similar in efficacy (Fig. 17).

**3.6.2. Impact of the concentration of HTM carriers.** The results indicate that  $V_{\text{OC}}$  (1.482 V) and  $J_{\text{SC}}$  ( $22.575 \text{ mA cm}^{-2}$ ) remain almost unchanged with increasing  $N_{\text{A}}$ . This stability arises because these parameters are primarily governed by the absorber's intrinsic optoelectronic properties, including bandgap, absorption coefficient, and carrier lifetime which are not significantly affected by moderate changes in the  $\text{MoO}_3$  HTL doping level. Consequently, carrier generation, separation, and transport within the absorber remain stable, in agreement with previous simulation studies on the limited effect of HTL doping on  $V_{\text{OC}}$  and  $J_{\text{SC}}$ . However, the FF shows a slight improvement, rising from 90.39% to 90.73% as  $N_{\text{A}}$  increases. The improvement is probably caused by increased hole transport efficiency and reduced series resistance at the HTL, owing to higher doping levels, enabling better charge extraction. The PCE rises from 30.26% to 30.36%, plateauing above a doping concentration of  $10^{15} \text{ cm}^{-3}$ .

**3.6.3. Impact of the concentration of ETM carriers.** Fig. 18 illustrates the influence of the ETL donor doping density ( $N_{\text{D}}$ ) on the photovoltaic performance of solar cells utilizing  $\text{TiO}_2$ ,



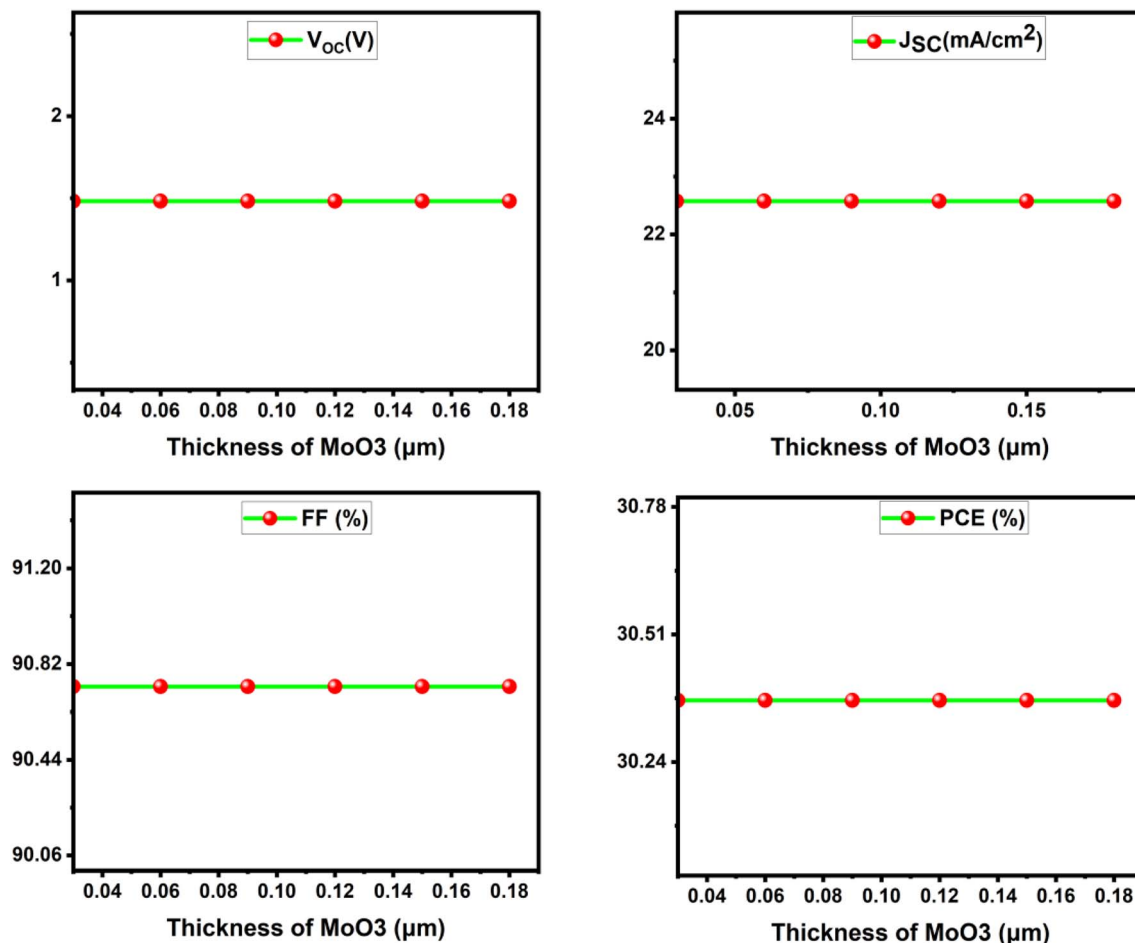


Fig. 16 Influence of MoO<sub>3</sub> layer thickness on the solar cell photovoltaic characteristics.

ZnO, and WS<sub>2</sub>. TiO<sub>2</sub> demonstrates consistent characteristics at all doping levels, maintaining a steady PCE of 30.41%, thus affirming its durability. Furthermore, AZnO shows a slight improvement in fill factor and efficiency as  $N_D$  increases, achieving a maximum power conversion efficiency of 30.48%. However, WS<sub>2</sub>, with a maximum efficiency of 25.71%, demonstrates poorer and more doping-sensitive performance. In contrast  $V_{OC}$  is mainly determined by the absorber bandgap and the splitting of the quasi-Fermi levels, which are controlled by carrier generation and recombination within the absorber. Since ETL doping does not directly affect these intrinsic mechanisms,  $V_{OC}$  remains unchanged. Similarly,  $J_{SC}$  is governed by photon absorption and the diffusion/collection of photogenerated carriers in the absorber. ETL doping does not alter the absorption spectrum or the intrinsic carrier generation, so  $J_{SC}$  also stays constant (Fig. 19).

### 3.7. Impact of series resistance on performance

The series resistance ( $R_S$ ) in a solar cell generally arises from three sources: carrier transport within the emitter and base layers, contact resistance at the metal–semiconductor

interfaces, and the resistance of the front and rear metallic contacts. Minimizing  $R_S$  is crucial, as high values cause internal voltage drops that reduce the fill factor (FF) and overall power conversion efficiency (PCE). Excessive resistive losses can significantly reduce the fill factor. In the current investigation, when  $R_S$  escalates from 0 to 6  $\Omega \text{ cm}^2$ ,  $V_{OC}$  and  $J_{SC}$  stay rather stable throughout all ETLs, however, the FF and PCE diminish gradually. TiO<sub>2</sub> and AZnO show excellent starting efficiencies of 30.93% and 30.80%, respectively, which decline to 27.83% and 27.72% at the maximum  $R_S$ . WS<sub>2</sub> starts at a lower PCE of 26.60%, dropping to 23.63%. This demonstrates that increasing series resistance affects device performance largely *via* lowering FF.

### 3.8. Impact of shunt resistance on performance

The shunt resistance ( $R_{SH}$ ) corresponds to leakage pathways through defects, pinholes, or imperfect interfaces. A low  $R_{SH}$  leads to significant losses in open-circuit voltage ( $V_{OC}$ ) and a decrease in FF, whereas a high  $R_{SH}$  ensures that the majority of photogenerated carriers contribute to power output. The influence of shunt resistance ( $R_{SH}$ ) on the photovoltaic performance





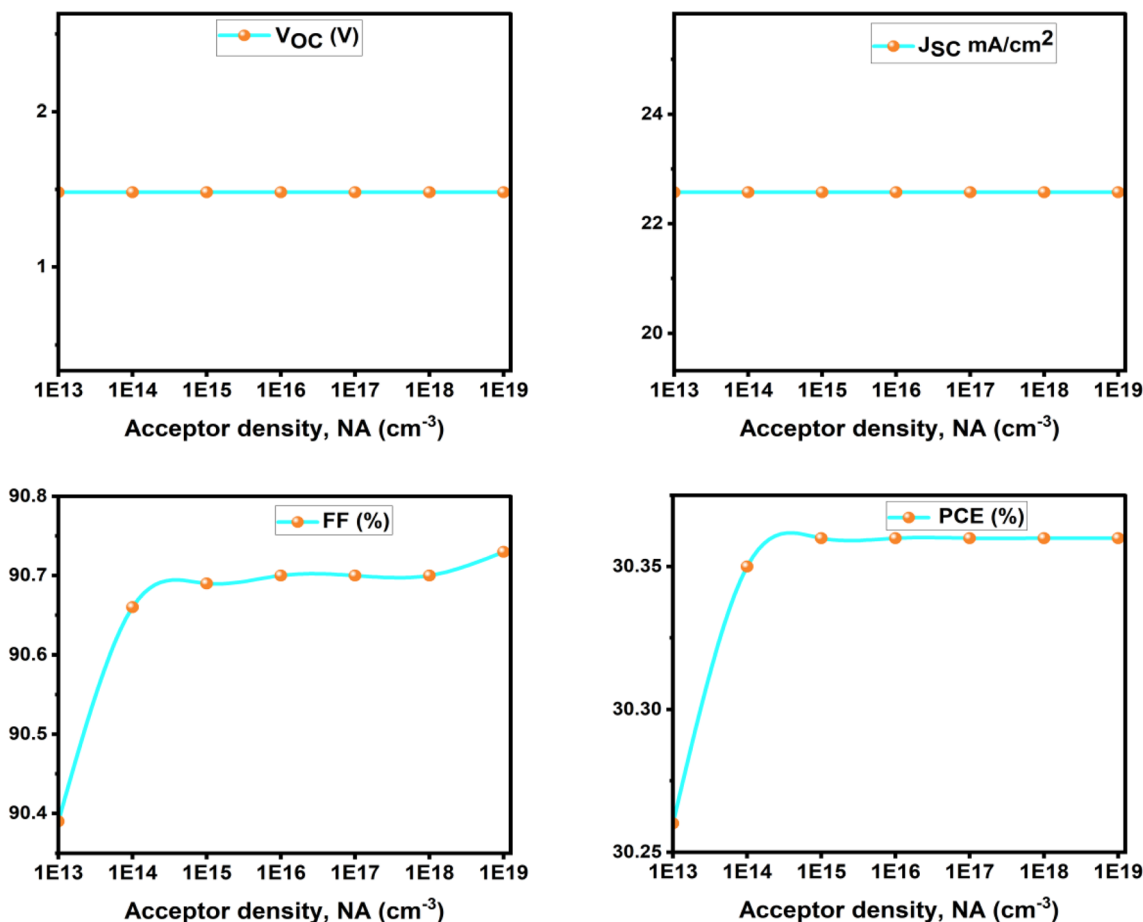


Fig. 17 Effect of  $\text{MoO}_3$  acceptor doping concentration ( $N_A$ ) on photovoltaic parameters.

of solar cells using AZnO,  $\text{TiO}_2$ , and  $\text{WS}_2$  as electron transport layers (ETLs) was studied. Fig. 20 shows that raising  $R_{SH}$  from 100 to  $900 \Omega \text{ cm}^2$  significantly improved FF and PCE across all configurations. This behavior is explained by suppressing leakage currents, which are usually linked to manufacturing flaws, and avoiding the junction using low-resistance shunt routes. In particular, when  $R_{SH}$  rose, FF for the AZnO-based device improved from 40.59% to 84.71%, and PCE improved from 13.59% to 28.88%. At  $R_{SH} = 900 \Omega \text{ cm}^2$ , the  $\text{TiO}_2$ - and  $\text{WS}_2$ -based cells showed comparable improvements, with final PCE values of 28.74% and 25.05%, respectively. The fill factor is the metric most sensitive to changes in shunt resistance, as seen by the relatively consistent  $V_{OC}$  and  $J_{SC}$  over the  $R_{SH}$  range.

### 3.9. Effect of temperature

One of the most difficult issues with PSC is guaranteeing its long-term stability, particularly at high temperatures. High temperatures can induce chemical and structural changes in perovskite materials, leading to a significant reduction in device performance. Furthermore, thermal stress may damage the integrity of the interfaces between distinct layers, causing greater charge carrier recombination and impeding charge transfer.<sup>28</sup> To better understand the thermal response of PSC in actual working situations, a rigorous performance study was

performed across a temperature range of 300 K to 400 K. Fig. 21. It has been demonstrated that increasing the temperature (from 300 to 400 K) reduces the  $V_{OC}$ , fill factor (FF), and PCE, while the  $J_{SC}$  remains essentially constant. This drop is mostly because of more recombination and energy loss at high temperatures, making removing charges and lowering the potential difference across the cell.  $\text{TiO}_2$  and AZnO have similar performance, with  $V_{OC}$  values of 1.48 V, PCEs surpassing 30% at 300 K, and strong thermal stability.  $\text{WS}_2$  had lower results ( $V_{OC}$  of 1.34 V, PCE  $\sim 25.7\%$ ) and more noticeable deterioration with temperature, indicating inefficient charge extraction and higher recombination. In contrast, the simulated  $J_{SC}$  remains nearly constant between 300 K and 400 K because photon absorption and carrier generation in the absorber are not significantly affected by temperature, while temperature mainly influences  $V_{OC}$  through the increase of the saturation current density.

### 3.10. Examination of the rates of recombination and generation

Elevating electrons from the  $B_V$  to the  $B_C$  causes holes to develop in the valence band, which in turn creates electron-hole pairs. This process is the essential mechanism for creating charge carriers in the substance. In SCAPS-1D, the generation rate  $G(x)$  is determined by the input photon flux  $N_{\text{phot}}(\lambda, x)$ ,



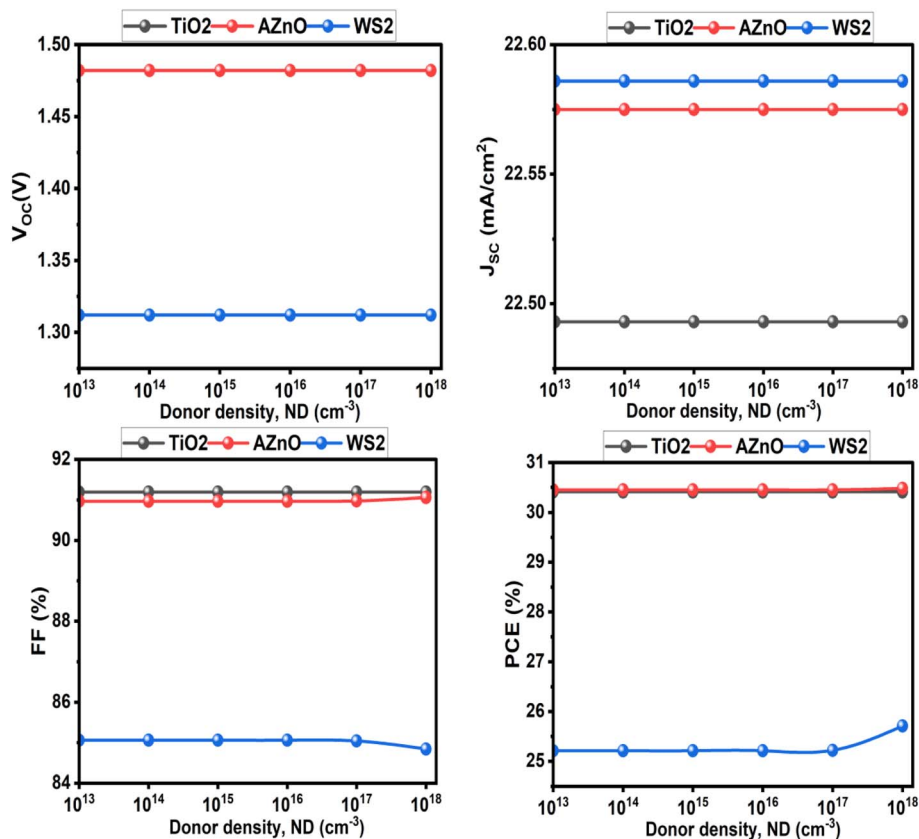


Fig. 18 Effect of ETM donor doping concentration ( $N_D$ ) on photovoltaic parameters.

which indicates the quantity of photons accessible for absorption at each depth  $x$  and wavelength  $\lambda$ . This photon flux is utilized to estimate the spatial generation profile within the absorber layer according to eqn (7):

$$G(\lambda, x) = \alpha(\lambda, x) \cdot N_{\text{phot}}(\lambda, x) \quad (7)$$

It is essential to integrate insights from carrier generation-recombination mechanisms and band structure studies to optimize absorber thickness, doping levels, and interface engineering, while selecting suitable ETLs and HTLs. This comprehensive knowledge enhances the efficiency, stability, and overall performance of  $\text{CaHfSe}_3$ -based solar cells. Fig. 22 illustrates carrier generation and recombination rates at various depths (0 to 1.1  $\mu\text{m}$ ) in three  $\text{CaHfSe}_3$ -based CP solar cells. Investigations indicate that generation rates for all devices peak between 0.15 and 0.3  $\mu\text{m}$ . In contrast, the recombination rate acts as a limiting factor, neutralizing these electron-hole pairs and preventing them from increasing the photocurrent. Carrier density and lifespan are the primary factors influencing the recombination rate. Moreover, defects present within the absorber and at its interfaces considerably increase the rate of electron-hole recombination. These imperfections, often caused by impurities, structural faults, or grain boundaries, lead to a non-uniform distribution of the recombination rate across the material. The PSC with  $\text{WS}_2$  and  $\text{AZnO}$  ETL had the

greatest recombination rates in the 1 to 1.1  $\mu\text{m}$  range, where  $\text{AZnO}$  as the ETL exhibited the highest rate. This occurs when additional electrons in the  $B_C$  bridge the  $E_g$  and join the  $B_V$ , becoming stable and taking the position of a hole.

### 3.11. Back contact effect on PV parameters

Eight distinct metals were used as rear electrodes (Table 3). In simulations for structure based on  $\text{FTO}/\text{AZnO}/\text{CaHfSe}_3/\text{MoO}_3$ , exhibiting work function values spanning from 4.65 to 5.70 eV, to assess the impact of the back contact Work function on device performance. The results are summarized in Fig. 23. It has been discovered that the PCE improves with an increasing work function, eventually reaching a saturation point of roughly 5.2 eV. At lower levels, the reduced PCE results from creating a Schottky barrier at the metal/absorber interface, which prevents effective hole extraction and promotes interfacial recombination. Furthermore, as the work function exceeds  $\sim 5.0$  eV, the energy alignment at the back contact becomes more favorable for hole transport, lowering barrier height and improving carrier extraction. This leads to a fast rise in efficiency, reaching a maximum of around 30.37%. Beyond this level, the device's performance plateaus, indicating that the contact performs ohmically. Significantly, while gold ensures superior device performance, it accounts for around 20% of the overall production cost in perovskite solar cells. Electrodes



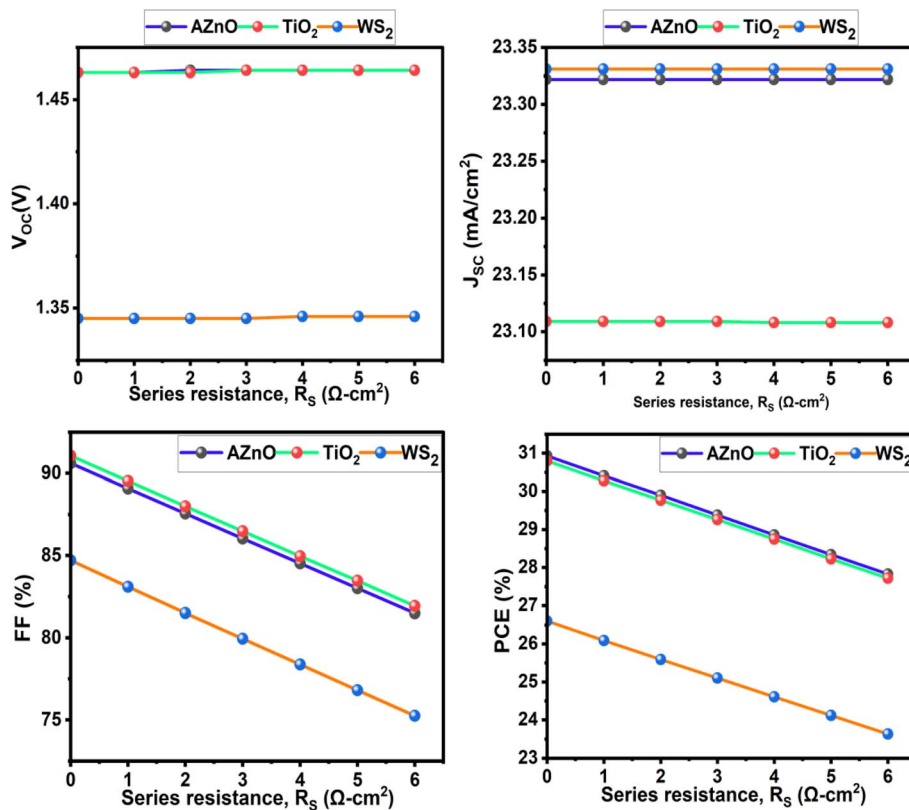


Fig. 19 The impact of series resistance on solar cell performance under varied ETLs.

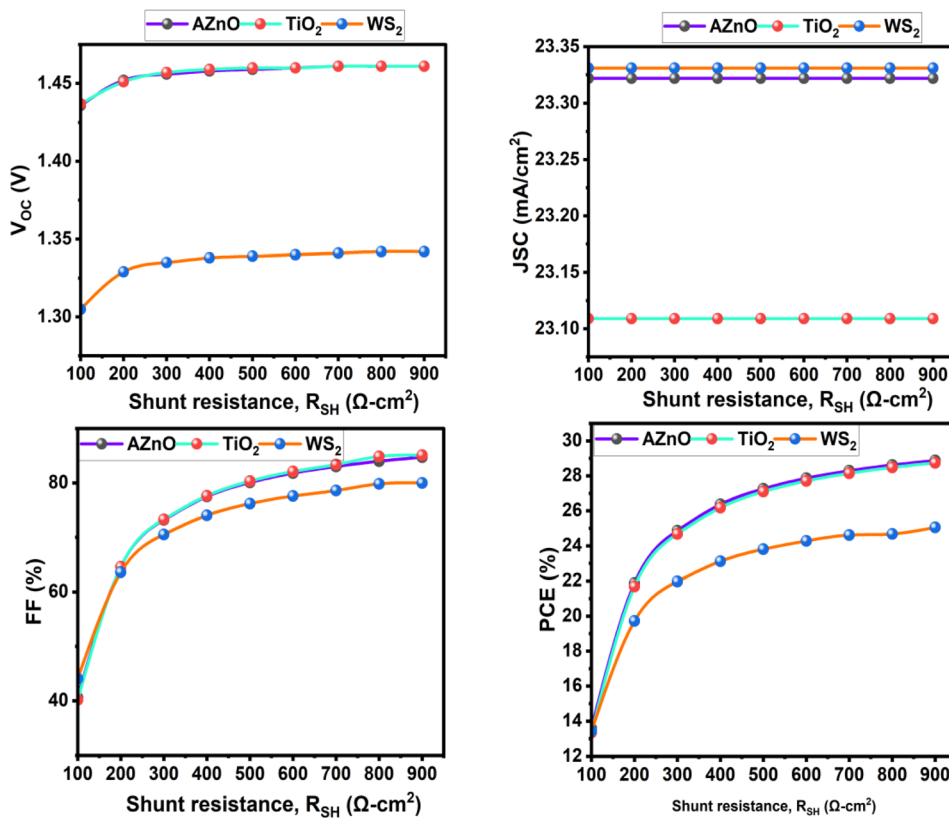


Fig. 20 Effect of  $R_{sh}$  on the PSCs parameters.

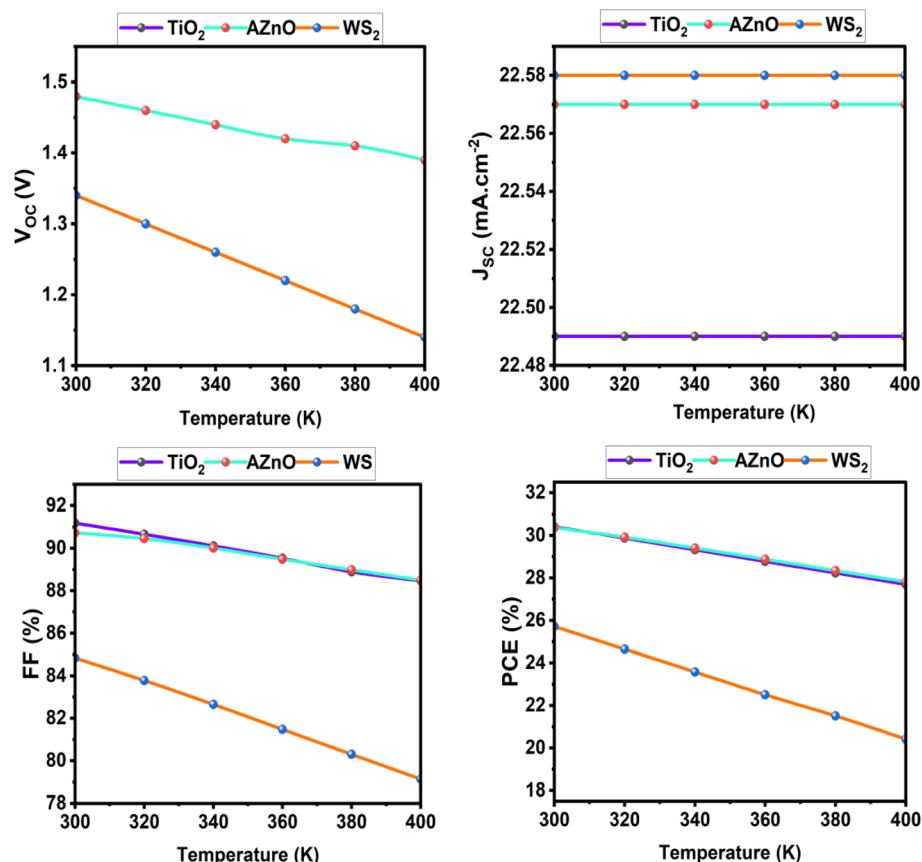


Fig. 21 Impact of temperature on solar cell performance using  $\text{TiO}_2$ ,  $\text{AZnO}$ , and  $\text{WS}_2$  as ETLs.

composed of Ni, Pd, and Pt provide cost-effective alternatives, demonstrating promising efficiency levels that render them feasible substitutes for Au without significantly compromising device performance.

### 3.12. Quantum efficiency and $J$ - $V$ properties

The current-voltage characteristics of the simulated devices are illustrated in Fig. 24(a). All three devices exhibited relatively high short-circuit current densities ( $J_{sc} \sim 22.49$ – $22.58 \text{ mA cm}^{-2}$ ), indicating that the  $\text{CaHfS}_3$  absorber effectively captures light and generates carriers. However, there are significant differences in overall current stability and open-circuit voltage ( $V_{oc}$ ). The cell utilizing  $\text{AZnO}$  as the ETL maintains a stable current plateau across a wide voltage range and achieves the highest  $V_{oc}$  ( $\approx 1.46 \text{ V}$ ). This suggests reduced interfacial recombination losses and excellent band alignment at the  $\text{AZnO}/\text{CaHfS}_3$  interface, indicating that  $\text{AZnO}$  is the most effective ETL among those studied. Fig. 24(b) shows how wavelength affects quantum efficiency (QE) for our investigation's three most successful devices. According to the data,  $\text{AZnO}$  and  $\text{WS}_2$  outperform  $\text{TiO}_2$  in the UV (300–360 nm) region, with QE values exceeding 90% compared to  $\text{TiO}_2$ ,

approximately 60%. This improvement may be attributed to the superior electrical and optical characteristics of  $\text{AZnO}$  and  $\text{WS}_2$ , such as their broad band alignment compatibility with  $\text{CaHfS}_3$  and high optical transparency in the ultraviolet region, resulting in more effective charge carrier extraction in the high-energy area. Within the visible spectrum (360–700 nm), all three ETL designs demonstrate virtually optimal quantum efficiency, with values around 100%. This suggests that the  $\text{CaHfS}_3$  absorber efficiently transforms visible light photons into charge carriers and that the ETLs retain good charge transport with negligible recombination losses throughout this range. However, after 700 nm, the QE starts to drop dramatically for all setups.  $\text{CaHfS}_3$ 's bandgap limits its ability to absorb low-energy photons in the near-infrared range, causing a noticeable drop at 770–800 nm.

### 3.13. Comparing SCAPS-1D results with earlier research

A comparison with previously reported perovskite-based devices is summarized in Table 4. The  $\text{FTO}/\text{TiO}_2/\text{CaHfSe}_3/\text{MoO}_3/\text{Au}$  and  $\text{FTO}/\text{AZnO}/\text{CaHfSe}_3/\text{MoO}_3/\text{Au}$  devices developed in this study exhibit outstanding photovoltaic performance, with  $V_{oc} \approx 1.52 \text{ V}$ ,  $J_{sc} \approx 23.17$ – $23.23 \text{ mA cm}^{-2}$ , and PCE values exceeding





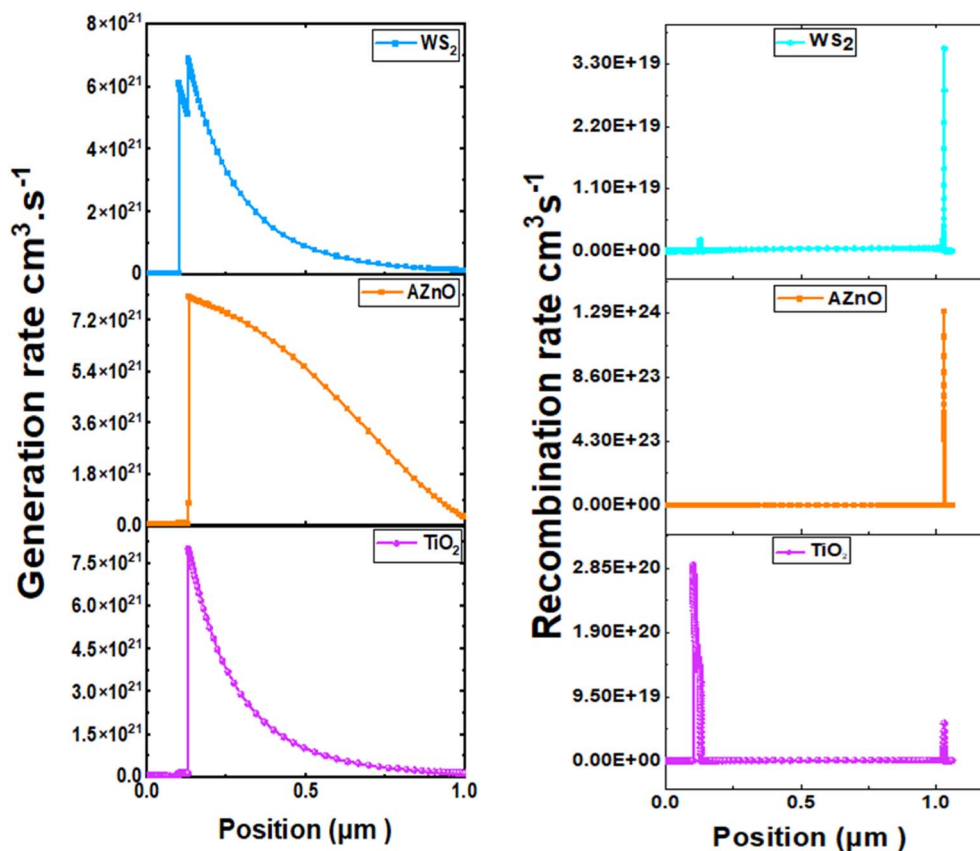


Fig. 22 Generation and recombination profiles in CaHfSe<sub>3</sub> absorber using TiO<sub>2</sub>, AZnO, and WS<sub>2</sub> as ETLs.

Table 3 The contacts used in the setups and their work function

Back electrode	Cu	Fe	C	Au	W	Ni	Pd	Pt
Work function (eV) (ref. 29)	4.65	4.82	5.00	5.30	5.22	5.50	5.60	5.70

32%. The TiO<sub>2</sub>-based structure achieves a slightly higher fill factor (91.41% vs. 91.02%) and overall efficiency (32.39% vs. 32.20%) compared to the AZnO-based device, reflecting lower resistive losses and more efficient charge extraction. These PCEs are significantly higher than those reported in previous studies, particularly for systems using CaHfSe<sub>3</sub> as the absorber layer. The top-performing FTO/TiO<sub>2</sub>/CaHfSe<sub>3</sub>/MoO<sub>3</sub>/Au device, achieving 32.39% efficiency, highlights the superior optoelectronic properties of CaHfSe<sub>3</sub> and its favorable energy alignment with MoO<sub>3</sub>. These results confirm the strong potential of the proposed materials and device architecture for high-performance, lead-free thin-film solar cells.

### 3.14. Validation against the ideal cell model

A comparison was made between the simulated photovoltaic properties of CaHfSe<sub>3</sub>-based solar cells and those of an ideal single-junction solar cell. The optimized combination, FTO/TiO<sub>2</sub>/CaHfSe<sub>3</sub>/MoO<sub>3</sub>/Au, attained a remarkable PCE of 32.39%, with a  $V_{OC}$  of 1.52 V, a  $J_{SC}$  of 23.17 mA cm<sup>-2</sup>, and an FF of 91.41%. This indicates that the results conform to the

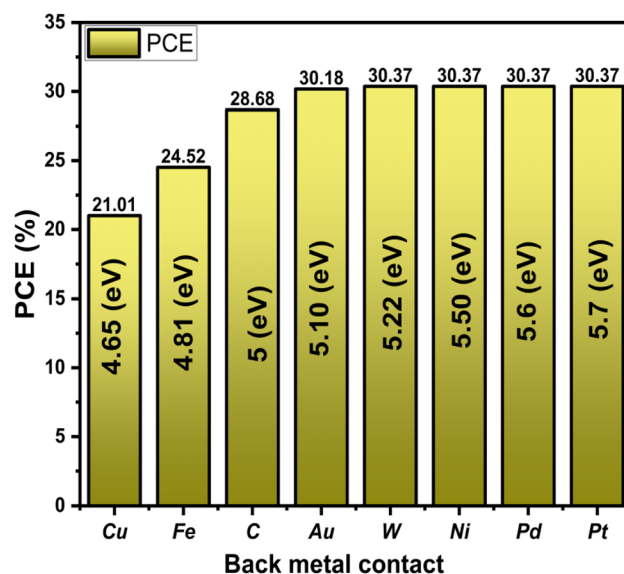


Fig. 23 Influence of the back electrode work function on solar cell PCE.

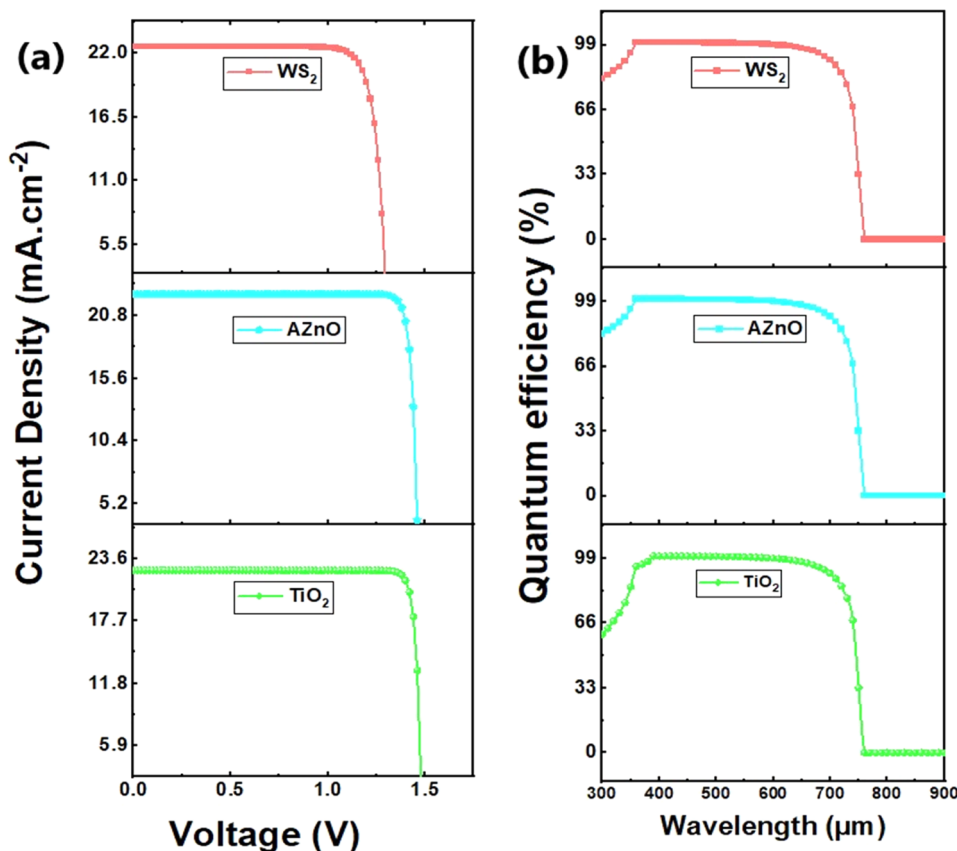


Fig. 24 (a)  $J$ - $V$  characteristics and (b) quantum efficiency for every device under study.

Table 4 Device comparison:  $V_{\text{OC}}$ ,  $J_{\text{SC}}$ , FF, and PCE

Structure	$V_{\text{OC}}$ (V)	$J_{\text{SC}}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)	Year	Ref.
FTO/ $\text{TiO}_2$ / $\text{CaHfSe}_3$ / $\text{MoO}_3$ /Au	1.52	23.169	91.41	32.39	—	—
FTO/ $\text{AZnO}$ / $\text{BaHfSe}_3$ / $\text{MoO}_3$ /Au	1.52	23.23	91.02	32.20	—	—
FTO/ $\text{WS}_2$ / $\text{BaHfSe}_3$ / $\text{MoO}_3$ /Au	1.34	23.22	84.85	29.12	—	—
FTO/ $\text{TiO}_2$ / $\text{CaHfSe}_3$ / $\text{NiO}_2$ /Au	1.30	20.62	83.78	22.58	2025	19
FTO/ $\text{TiO}_2$ / $\text{BaZrS}_3$ /SpiroOMeTAD/Au	0.70	22.00	79.40	12.42	2023	30
FTO/ $\text{TiO}_2$ / $\text{CaZrS}_3$ /CuO	0.60	35.73	80.88	17.53	2024	18

theoretical boundaries of an ideal single-junction solar cell.<sup>31</sup> These results demonstrate the great promise of  $\text{CaHfSe}_3$  as an absorber material for lead-free perovskite solar cells, since they approach the theoretical Shockley Queisser limit.

## 4. Conclusion

This makes our study unique as it intends to examine the photovoltaic characteristics of  $\text{CaHfSe}_3$  absorber material in state-of-the-art solar cells. We explored the potential of devices constructed FTO/ $\text{TiO}_2$ ,  $\text{AZnO}$  and  $\text{WS}_2$  layers with  $\text{CaHfSe}_3$ / $\text{MoO}_3$ /Au using SCAPS-1D simulations. We then analysed the effects of the absorber thickness, the density of defects in the absorber, carrier concentration in electron & hole transport layers, levels of acceptor doping, *etc.*, and how these factors impact the efficiency of the devices. The effects of  $R_s$  and  $R_{\text{SH}}$ ,

and temperature of operation in addition to other variables explored, were also examined in relation to overall photovoltaic performance. A detailed study of the band structure, carrier generation and recombination rates,  $J$ - $V$  characteristics, and quantum efficiency (QE) was presented herein. The optimized device structure FTO/ $\text{TiO}_2$ / $\text{CaHfSe}_3$ / $\text{MoO}_3$ /Au yielded a power conversion efficiency (PCE) of 32.39%, with a  $V_{\text{OC}}$  of 1.52 V,  $J_{\text{SC}}$  of 23.17  $\text{mA cm}^{-2}$ , and fill factor (FF) of 91.41%. In contrast, the FTO/ $\text{AZnO}$ / $\text{CaHfSe}_3$ / $\text{MoO}_3$ /Au structure had a PCE of 32.20% with near identical electrical properties. Overall, the results suggest the high optoelectronic quality of  $\text{CaHfSe}_3$ , and its compatibility with multiple ETLs. Additionally, cheap substitutes for gold in the back contact were examined, including carbon, with only modest losses in efficiency. Overall, this detailed and systematic work contributes to the understanding



of  $\text{CaHfSe}_3$ -based perovskite solar cells. It represents a potential pathway towards a lead-free, efficient, low-cost, and sustainable photovoltaic technology, and will support clean energy targets of the future.

## Conflicts of interest

The authors declare no conflict of interest.

## Data availability

The data will be available from the corresponding author on reasonable request. SCAPS-1D is available from <https://scaps.elis.ugent.be/>.

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