The Hole Transport Layer Material Optimization for an Efficient Lead-Free Double Perovskite Cs₂AgBiBr₆ Based Solar Cell by Numerical Simulation

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Lead-free double perovskites have recently emerged as a promising alternative material for solar cell applications, exhibiting encouraging optoelectronic properties, high environmental stability, and low toxicity. In this manuscript, we report the effect of different hole transport layer materials on the photovoltaic performance of lead-free double perovskite solar cells. Optimization of hole transport layers (HTLs) is performed by correlating the open-circuit voltage (V_{oc}) with the built-in potential (V_{bi}). It is revealed from the simulation results that higher V_{bi} resulted in higher V_{oc}. Also, it is found that for proper selection of HTLs, E_{V_HTL} (valence band maximum of HTL) and φ_{BC} (work function of back contact) should not be much deeper than E_{V_PVK} (valence band maximum of a double perovskite layer) to avoid V_{bi} loss. In the present study, FTO/TiO₂/Cs₂AgBiBr₆/HTLs/Cu device was designed, and Solar Cell Capacitance Simulator (SCAPS-1D) was used for one-dimensional simulation and analysis. An active layer of 0.3 µm was used for the present work. Photovoltaic power conversion efficiency (PCE), V_{oc}, J_{sc}, and FF were obtained using numerical simulation. The most suitable hole transport layer material was found to be Spiro-OMeTAD. Moreover, under optimized conditions, the device PCE increased to 3.75 %. The optimized photovoltaic performance of the device is as follows: open-circuit voltage $V_{oc} = 7.2412$ V, short-circuit current density $J_{sc} = 8.02965$ mA/cm², and fill factor FF = 6.45 %. Overall, the encouraging simulation results achieved in this study will provide insightful guidance for replacing the commonly used carcinogenic Pb-based perovskite with eco-friendly, highly efficient inorganic perovskite solar cells.

Keywords: Double perovskite, ETL, HTL, SCAPS-1D, Fill factor, Quantum efficiency.

1. INTRODUCTION

The lead (Pb) based hybrid perovskite materials have been used extensively for solar cells because of the high-power conversion efficiency of around 25 % [1]. But, due to the toxicity of lead and the difficulty of the fabrication process of those cells, the commercial applications of such cells have been pushed back. Generally, a Perovskite Solar Cell (PSC) should include an electron transport layer (ETL) and a hole transport layer (HTL) to maximize its power conversion efficiency (PCE) by extracting and transporting photo-generated electrons, modifying the interface, aligning the interfacial energy level, and minimizing the charge recombination in PSC, as well as improving hole extraction and selectively blocking electrons to diminish electron-hole recombination on the anode.[2] The volatility of the organic cation is considered to be a significant contributor to instability, which should be improved using inorganic cations.[3] For these reasons, the search for alternative inorganic perovskites employing less toxic metals is of paramount importance[4-6]. In this landscape, double perovskites have recently emerged as a promising alternative exhibiting encouraging optoelectronic properties, high environmental stability, and low toxicity. In particular, the double perovskite Cs₂AgBiBr₆ has been the subject of much fundamental material characterization and initial application in photodetectors and photovoltaic devices [7-14].

In this present study, we have studied the solar cell device with cesium-based inorganic absorbing material Cs₂AgBiBr₆ for the best photovoltaic performance under the optimum absorbing layer thickness. The titanium dioxide (TiO₂) has been used for ETL and four different hole transport layer materials are investigated.

2. METHODOLOGY

SCAPS-1D is a window-oriented one-dimensional solar cell capacitance simulator developed at the Department of Electronics and Information Systems of the University of Gent, Belgium [15]. The program is written in the C programming language. Various profiles including grading, generation, recombination, and defects of device architecture can be calculated using this simulation program. Poison's equation, transport equation, and continuity equation are the three mainly used differential equations in this simulator to calculate parameters such as diffusion length of electron and holes ($L_{n,p}$), open-circuit voltage (V_{oc}), solar cell light generated current density (J_{sc}), fill factor (FF) and photo-conversion efficiency (PCE). The effects of different factors like a medium (dark or light), illumination, working point temperature, and voltage can also be observed by varying inputs using this computational platform.

2.1 Architecture of the Devices

The structure of soda-lime glass (SLG)/FTO/ETL/Cs₂AgBiBr₆/HTL/copper (Cu) solar cell is shown in Fig. 1, where Spiro-OMeTAD, CuI, NiO, CuSCN are used as *p*-type HTLs over the Cu back contact, Cs₂AgBiBr₆ is a *p*-type absorber layer, TiO₂ is an *n*-type ETL, and FTO is an *n*-type window layer. It is a

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solid-state planar heterojunction *p*-i-*n* solar cell with *p*-type Cs₂AgBiBr₆ sandwiched between *n*-type ETL and *p*-type HTL. SLG is over FTO, and light fell on the SLG side. Both arrangements had two interfacial layers-HTL/absorber layer and the absorber layer/ETL. The band-gap alignment of the device is shown in Fig. 1.
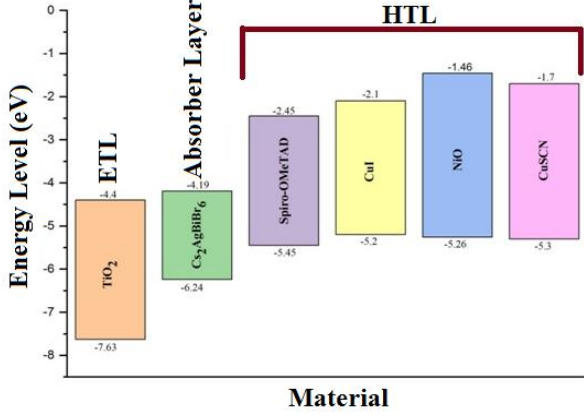

Fig. 1 – Band alignment

2.2 Simulated Parameters

The material parameters used in this simulation are listed in Table 1.

Table 1 – SCAPS-1D input material parameters used in the solar cell simulation for FTO, ETL and Cs₂AgBiBr₆

Parameters	Window layer FTO	ETL TiO₂	Absorber layer Cs₂AgBiBr₆
Thickness, µm	0.2	0.3	0.1-1
Bandgap (E_g), eV	3.2	3.23	2.05
Electron affinity (χ), eV	4.4	4.26	4.19
Relative permittivity (ε_r)	9.0	9.0	5.80
CB effective density of states (N_c), cm⁻³	2.2E+18	2.0E+18	1.0E+16
VB effective density of states (N_v), cm⁻³	1.8E+19	1.8E+20	1.0E+16
Electron mobility (μ_n), cm²·V⁻¹·s⁻¹	20	4	11.81
Hole mobility (μ_p), cm²·V⁻¹·s⁻¹	10	2	0.49
Donor density (N_d), cm⁻³	1.0E+18	6.0E+19	1.0E+19
Acceptor density (N_a), cm⁻³	0	0	1.0E+19
Defect density (N_t), cm⁻³	1.0E+15	1.0E+18	9.1E+16

The values were chosen from the literature and the previous simulation works [16, 17]. The default value of temperature is taken as 300 K with standard illumine-

tion of AM1.5G. All simulations are run at light medium, 1000 W·m⁻² illumination, 1 Ohm·cm² series resistance, and 1000 Ohm·cm² shunt resistance. Electron and hole thermal velocities are kept constant at 10⁷ cm·s⁻¹. The band-to-band radiative recombination coefficient value is taken as 2.3·10⁻⁸ cm³·s⁻¹ initially, which is varied later [18]. Neutral type and donor type defects are considered for HTL and absorber layer, respectively. But for both ETL and window layers, acceptor type defects are considered. The absorber layer and ETL have variable total defect density (N_t), whereas HTL has fixed N_t [19]. All interfacial layers (HTL/absorber layer and absorber layer/ETL) have neutral type defects and variable trap densities. For Cu back contact, work function was 5 eV, and thermionic emission/ surface recombination velocities for electrons and holes are 10⁵ cm·s⁻¹ and 10⁷ cm·s⁻¹, respectively. The optical absorption constant, α ($h\upsilon$), for the perovskite layer is set by the new "Eg-sqrt" model, and the details of the model are taken from various literatures [11-20].

Table 2 – SCAPS-1D input material parameters used in the solar cell simulation for different HTL materials

Parameters	HTL1 Spiro-OMeTAD	HTL2 CuI	HTL3 NiO	HTL4 CuSCN
Thickness, µm	0.3	0.3	0.3	0.3
Bandgap (E_g), eV	3.0	3.1	3.8	3.6
Electron affinity (χ), eV	2.45	2.1	1.46	1.7
Relative permittivity (ε_r)	3.0	6.5	11.7	10
CB effective density of states (N_c), cm⁻³	2.2E+19	2.2E+19	2.5E+20	2.2E+19
VB effective density of states (N_v), cm⁻³	1.8E+19	1.8E+19	2.5E+20	1.8E+19
Electron mobility (μ_n), cm²·V⁻¹·s⁻¹	2.0E-4	1.0E+2	2.8	1.0E+2
Hole mobility (μ_p), cm²·V⁻¹·s⁻¹	2.0E-4	4.39E+1	2.8	2.5E+1
Donor density (N_d), cm⁻³	0	0	0	0
Acceptor density (N_a), cm⁻³	1.0E+18	1.0E+18	1.0E+18	1.0E+18
Defect density (N_t), cm⁻³	1.0E+14	1.0E+14	1.0E+15	1.0E+14

3. RESULTS AND DISCUSSION

3.1 Hole Transport Layers Effect on the *J-V* Curve

The device configuration soda-lime glass (SLG)/ FTO/ETL/Cs$_2$AgBiBr$_6$/HTLs/Copper (Cu) was simulated by employing different HTL materials one by one and the resulting *J-V* curve has been shown in Fig. 2. The effect of various hole transport materials on the device performance of DPSC is analyzed. Based on the conduction band and valence band energy level different HTLs are arranged and shown in Fig. 1. It can be suggested that the lowest V_{oc} is obtained by NiO and the highest open-circuit voltage is obtained by Spiro-OMeTAD which significantly increases it's η from 2.37 % to 3.75 %. Fig. 2 shows the resulted current-voltage (*J-V*) curve of the hole transport layers used in the simulation of lead-free DPSC.
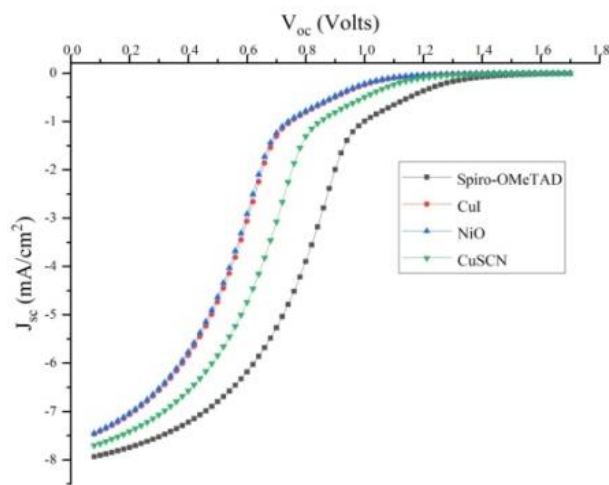

Fig. 2 – *J-V* curve for different HTL materials

It is evident from the *J-V* curve that Spiro-OMeTAD shows the higher V_{oc} as well as J_{sc}. On the contrary, NiO shows the lowest V_{oc} and J_{sc}. The highest values of V_{oc} and J_{sc} of Spiro-OMeTAD are attributed to the better alignment with the corresponding layers. Also, the better performance of Spiro-OMeTAD could be related to lower series resistance and high shunt resistance in the device.

3.2 Hole Transport Layers Effect on the Quantum Efficiency

It can be observed from Fig. 3 that a quite low QE is observed for the NiO HTL layer. The lower QE of NiO is due to its lower band gap as most of the carriers are absorbed in the hole transport layer instead of the absorber layer. Due to this the absorption of photons, as well as carrier generation, decreases in the absorber layer and as a result, PCE in the case of NiO is lowest as compared to other HTL materials. The higher charge collection probability in Spiro-OMeTAD is one of the reasons for better QE as compared to other HTL materials. On the other hand, no significant differences are observed on the quantum efficiency curve by changing the HTL material. It is clear from our simulation

results that the reduced QE response at longer wavelengths indicates the lower absorption of longer wavelengths and low diffusion length of carriers. Also, from Fig. 2 and Fig. 3, it is observed that Spiro-OMeTAD shows higher photovoltaic performance, and hence for future optimization, this is preferred as a hole transport layer material.
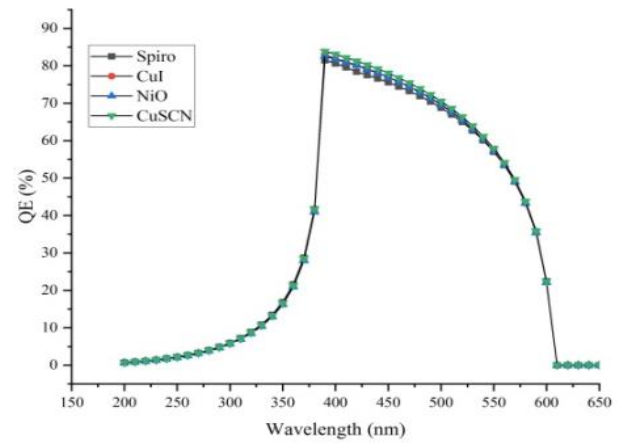

Fig. 3 – Quantum efficiency (QE) vs wavelength (λ) curve

4. CONCLUSIONS

In this research work, lead-free PSCs with the double perovskite (Cs$_2$AgBiBr$_6$) as the absorber layer is investigated through SCAPS-1D simulation. The configuration of the PSC is glass substrate/FTO/ETL/ Cs$_2$AgBiBr$_6$/HTL/Cu. The simulation results reveal that the active material performance depends upon the type of HTL material. The optimal HTL layer material is found to be Spiro-OMeTAD for the double perovskite Cs$_2$AgBiBr$_6$ material. It is obtained from the simulation results that to attain higher V_{oc} and PCE the proper selection of HTL material is a crucial factor. The best spectral response for the double perovskite material was found to be at 390 nm. This concludes that the material is active in the visible region of the solar spectrum. The variation of the series resistance affects the performance of the solar cell as can be realized from the results. The present proposed device architecture is a regular planar structure and the same may be studied for the effect of other device parameters on the performance of mixed halide double perovskite materials. The downward trend exhibited by FF with an increase in absorber layer thickness can be explained by the less effective transportation of electron-hole pair through the cell with higher recombination. After comprehensive optimization, the device photovoltaic performance elevates up to $V_{oc} = 7.24$ Volts, $J_{sc} = $ mA/cm^2, and $\eta = 3.75\%$. Due to the wideband gap of the double-perovskite layer, this simulation study will help to design a lead-free perovskite-based tandem solar cell.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Оптимізація матеріалу транспортного шару дірок для ефективного сонячного елемента на основі безсвинцевого подвійного перовскіту Cs₂AgBiBr₆ за допомогою чисельного моделювання

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Безсвинцеві подвійні перовскіти нещодавно стали перспективним альтернативним матеріалом для застосування в сонячних елементах, демонструючи обнадійливі оптоелектронні властивості, високу екологічну стабільність і низьку токсичність. У статті повідомляється про вплив різних матеріалів транспортного шару дірок на фотоелектричні характеристики сонячних елементів на основі безсвинцевих подвійних перовскітів. Оптимізація транспортних шарів дірок (HTLs) здійснюється шляхом кореляції напруги холостого ходу (V_{oc}) із вбудованим потенціалом (V_{bi}). Результати моделювання показали, що вище значення V_{bi} призвело до більшого значення V_{oc}. Також встановлено, що для правильного вибору HTLs, E_{V_HTL} (максимум валентної зони HTL) і φ_{BC} (робота виходу зворотного контакту) не повинні бути набагато глибшими, ніж E_{V_PVK} (максимум валентної зони подвійного перовскітного шару), щоб уникнути втрат V_{bi}. У дослідженні було розроблено пристрій FTO/TiO₂/Cs₂AgBiBr₆/HTLs/Cu, і його одновимірне моделювання та аналіз було проведено симулятором ємності сонячних елементів (SCAPS-1D). Для роботи використано активний шар 0,3 мкм. Ефективність перетворення фотоелектричної енергії (PCE), V_{oc}, J_{sc} і FF були отримані за допомогою чисельного моделювання. Виявлено, що найбільш підходящим матеріалом транспортного шару дірок є Spiro-OMeTAD. Крім того, в оптимізованих умовах PCE приладу зросла до 3,75 %. Оптимізовані фотоелектричні характеристики пристрою такі: напруга холостого ходу $V_{oc} = 7{,}2412$ В, густина струму короткого замикання $J_{sc} = 8{,}02965$ мА/см² і коефіцієнт заповнення FF = 6.45 %. В цілому, обнадійливі результати моделювання, отримані в даному дослідженні, дадуть вказівки щодо заміни широко використовуваного канцерогенного перовскіту на основі Pb екологічно чистими, високоефективними неорганічними перовскітними сонячними елементами.

Ключові слова: Подвійний перовскіт, ETL, HTL, SCAPS-1D, Коефіцієнт заповнення, Квантова ефективність.