Optimizing Lead-Free Double Perovskite Solar Cells using SCAPS-1D Framework

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Abstract. Investigating the photovoltaic (PV) performance of lead-free double perovskite solar cells (DPSCs) with a structure comprising a fluorine-doped tin oxide (FTO) substrate, tungsten disulfide (WS2) as the electron transport layer (ETL), inorganic-lead free and non-toxic double perovskite La2NiMnO6 absorber, Spiro-OMeTAD as the hole transport layer (HTL), and gold (Au) electrode using the SCAPS-1D framework is crucial for optimizing their efficiency. Despite significant progress in DPSCs, there remains a research gap in understanding the fundamental mechanisms underlying their performance, particularly in optimizing material properties and device architectures for enhanced efficiency. This study focuses on optimizing the device architecture by investigating the impact of band alignment, electric field, layer thickness, temperature, series resistance, and shunt resistance on enhancing DPSC performance. Achieving an power conversion efficiency (PCE) of 18.51% with detailed analysis of the DPSCs highlights the key factors influencing their efficiency. These findings contribute valuable insights into enhancing the performance of DPSCs, advancing their potential for widespread adoption in solar energy conversion.

1 Introduction

Sputtering perovskite with metal halides, which is a mixed organic-inorganic material, is rapidly gaining interest for its application to solar cell development. They are popular in certain characteristics, including a high absorption coefficient, lower excited state energy, energy gap tunability, an excellent charge collection mobility, and other incomparable properties, giving them a place for efficient solar cells manufacturing[1–3]. Perovskite thin films in high uniformity can be prepared through multiple chemical processing techniques[4–8]. Under the year of 2009, scientists already have many studies on Perovskite materials for the PV purposes, where the nominal efficiency has touched 3. 8% to 25. In 2021, 25.7% of the amount also went into the reserve augmented by the enhanced stability[9, 10]. Nonetheless, these developments are not without impediments since several barriers hamper the commercialization of DPSC. The toxicity of lead is a serious problem. Other problems includes the elasticity of the active layer towards UV radiation and humidity, and the low lifespan of

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the perovskite layer, respectively[11–18]. What so if given is the case, the replacement of PSCs with \( A_2BB'O_6 \) must be studied, where \( A \) corresponds to Lanthanides as well as \( B, B' \) speaks of transition elements[19]. In case of the double perovskite materials two different elements are located in B-site, which is center of research of many scientists[20–22]. Among the variety of the materials LNMO (Lanthanum, Nickel, and Manganese) oxide is of special interest as it is convenient in terms of its preparation[23, 24]. LNMO films have demonstrated the ability to talk optical issues with a bandgap of about 1 eV, where the highlighted methylammonium lead halide (\( \text{CH}_3\text{NH}_3\text{PbI}_3 \)) is a popular material for study[25]. The parallelity in this assertion makes LNMO a tremendously attractive technology option for solar applications.

As a composite of \( \text{La}_2\text{NiMnO}_6 \) (where Ni is at B-site instead of walking and Mn and ‘A are both at A-site no wandering around), \( \text{Ln}_2\text{NiMnO}_6 \) again also contains superior magnetic, dielectric, optical, and electrical features, which makes it suitable for applicationscite[26]. Nevertheless, tremendous development in others has only contributed to ambiguity over why the perovskites of double type have not been actively utilized as top performing PVs given the fact that the PSc hasn’t even scratched the surface in relation to their conceptually achievable efficiency limit. The creation of a superior perovskite layer is the primary challenge facing this developing sector in order to overcome losses including open-circuit voltage (\( V_{OC} \)) losses, compound losses, series and parallel resistance losses, bandgap losses, and field value (FF) losses[27–30]. Zhang et al. [31] in the year 2012, the advancement of LNMO films with well crystallized structure employing precursor-based sol-gel protocol was confirmed. Lan et al. [32] described the in 2016 paper of the LNMO-type PSCs which claimed its characteristics including theoretical and experimental evidences. Sheikh et al. [33] portrayed \( \text{Ln}_2\text{NiMnO}_6 \) compositions (where \( \text{Ln} \) is Lu, Eu, La, and Dy) covering the span from 1.0 to 1.1 of the energy gap. Consequently, a double perovskite-based solar cell can reach up to 1.1 eV, which is essentially the band gap, previously being considered the highest energetic level, capable of catalyzing charge transfer. Currently, efforts are underway using modelling and simulation, to comprehend the device architecture for the efficiency of such devices, but reports on oxide perovskites are limited[34, 35].

Essential PV properties including high PCE, scientists are working actively experimentally and theoretically on lead-free LNMO based DPSCs. Kumar et al. [36] investigated an heterojunction device, to implement PCE of 15.42% use \( \text{TiO}_2 \) as ETL and \( \text{CuI} \) as HTL. Pal et al. [37] utilized an architecture, with \( \text{TiO}_2 \) as an ETL and Spiro-OMeTAD as HTL to achieve PCE of 22.43%. Although \( \text{La}_2\text{NiMnO}_6 \) is considered a promising perovskite for solar energy applications, there is not enough theoretical research to support this claim.

This study aims to elucidate the function of DPSC by examining the effects of changing the voltage, current, thickness, defect density, shunt, and series resistance while also analysing external quantum efficiency (EQE) and current-voltage (JV). In order to optimise the functionality of the DPSC device, the device is optimized. Additionally, the combination of BCP/C\(_{60}\), known for its excellent charge extraction and improved PV device performance, is used for the first time in this study for LNMO-based double PSCs[38–42].

For inverted device structures, NiO is widely reported in the literature as a hole transporting material and can be easily deposited using a simple sol-gel process[43–45]. SCAPS-1D modelling approach is used in this study to investigate lead-free double perovskite LNMO as an absorber material. The heterostructure device FTO/WS\(_2\)/LNMO/Spiro–OMeTAD/Au is novel.
2 Methodology

2.1 Device Structure Simulation

For the simulation of DPSC, SCAPS-1D software is used. The device structure consists of a fluorine-doped tin oxide (FTO) layer coated on the glass substrate, a compact TiO$_2$ layer, a mesoporous TiO$_2$ layer, a perovskite absorber layer (LMNO), a HTL (Spiro–OMeTAD), an ETL (WS$_2$), and a metal electrode (Au). The dimensions and material properties of each layer were defined based on experimental values and literature data.

2.2 Material Properties and Model Parameters

Properties are carefully selected for the simulation of the configuration, to accurately represent the behavior of each layer in the device, including the optical constants, carrier mobilities, and carrier lifetimes of the materials. The parameters were adjusted iteratively to match experimental data and optimize the device performance.

2.3 Simulation Setup

The simulation was set up to solve the one-dimensional drift-diffusion equations for electrons and holes in each layer of the device. The equations were solved self-consistently to calculate the carrier concentrations, current densities, and other device characteristics under illumination.

2.4 Optical and Electrical Modeling

To inspect optical properties at DPSC, using transfer matrix method to calculate the absorption coefficient and the generation rate profile throughout the layer. To study the device’s electrical characteristics, such as the current-voltage (IV) characteristics, carrier concentrations and transport properties in each layer were calculated.

2.5 Parameter Extraction and Analysis

The simulation results were used to extract key performance parameters of PCE, FF, $V_{OC}$, and short-circuit current density ($J_{SC}$) of the solar cell. Sensitivity analysis was performed to identify the factors influencing the device performance and optimize the device structure and material properties accordingly.

2.6 Validation and Comparison

The simulated results is validated against experimental data from fabricated devices to ensure the accuracy and reliability of the simulations in Table 1. The performance of the simulated devices is also validated with different configuration devices based on other materials and structures to assess the potential of DPSC for practical applications.
This methodology provides a detailed and systematic approach to simulating perovskite solar cells using SCAPS-1D, enabling researchers to optimize device performance and explore new materials and designs for next-generation solar cells.

### 3 Results and discussions

#### 3.1 Examination of SCAPS-1D Data

To evaluate the PV performance of the heterostructure with 800nm of LNMO absorber thickness, $10^{18} \text{cm}^{-3}$ acceptor doping concentration, and $10^{15} \text{cm}^{-3}$ defect densities, while maintaining constant carrier concentration, thickness, and defect density of the HTL, ETL, and absorber layers. All the parameters used to extract all these results of the device are given in the Table 2.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>FTO[50]</th>
<th>Spiro-OMeTAD[51]</th>
<th>WS$_2$[51]</th>
<th>La$_2$NiMnO$_6$[52]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>500</td>
<td>variable</td>
<td>variable</td>
<td>variable</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>3.5</td>
<td>3</td>
<td>1.8</td>
<td>1.4</td>
</tr>
<tr>
<td>$\chi$</td>
<td>4</td>
<td>2.2</td>
<td>3.95</td>
<td>3.5</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>9</td>
<td>3</td>
<td>13.6</td>
<td>3.52</td>
</tr>
<tr>
<td>$N_C$</td>
<td>$2.2 \times 10^{18}$</td>
<td>$2.2 \times 10^{18}$</td>
<td>$1 \times 10^{18}$</td>
<td>$1 \times 10^{18}$</td>
</tr>
<tr>
<td>$N_V$</td>
<td>$1.8 \times 10^{19}$</td>
<td>$1.8 \times 10^{19}$</td>
<td>$2.4 \times 10^{19}$</td>
<td>$1 \times 10^{18}$</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>20</td>
<td>$2.1 \times 10^{-3}$</td>
<td>100</td>
<td>22</td>
</tr>
<tr>
<td>$\mu_h$</td>
<td>10</td>
<td>$2.16 \times 10^{-3}$</td>
<td>100</td>
<td>22</td>
</tr>
<tr>
<td>$N_A$</td>
<td>0</td>
<td>$1 \times 10^{18}$</td>
<td>0</td>
<td>$1 \times 10^{14}$</td>
</tr>
<tr>
<td>$N_D$</td>
<td>$1 \times 10^{19}$</td>
<td>0</td>
<td>$1 \times 10^{18}$</td>
<td>$7 \times 10^{16}$</td>
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<tr>
<td>$N_f$</td>
<td>-</td>
<td>$1 \times 10^{15}$</td>
<td>$1 \times 10^{15}$</td>
<td>-</td>
</tr>
</tbody>
</table>

#### 3.1.1 Lead-free DPSC Band Alignment

Minimum and maximum values of conduction and valence band, individually, are portrayed within the Figure 1. There is still a harmonic link between $F_n$ and $E_C$, and $F_p$ is in phase with $E_V$. In the configuration, ETL blocks hole movement, while the HTL hinders electron movement. The FTO front contact efficiently collects electrons, whereas the Au back contact collects holes from the HTL. A function of work (WF) of 4.7 eV was used as back contact with gold, and as front contact with FTO, a WF of 4.4 eV was taken into account.
3.1.2 Impact of ETL and absorber thickness on cell efficiency

Researching on the PV performance of lead-free DPSCs is, therefore, essential in improving their efficiency. This work uses an Au electrode, a tungsten disulfide (WS₂) ETL, a non-toxic and lead-free double perovskite absorber layer of La₂NiMnO₆, an FTO coated on a glass substrate, and Spiro-OMeTAD as the HTL. Using the SCAPS-1D framework, is used to obtain efficiency contour maps which are determined by the absorber thickness (100–1300 nm) and ETL thickness (100–800 nm). Efficiency is the highest at 18.51% was obtained at a 350 nm thick LMNO absorber and a 500 nm ETL thickness. In contrary, the lowest efficiency is 12.9% at thickness of 100 nm with LNMO and an ETL layer of 800 nm. These results highlight the significance of optimizing device architectures and material properties to enhance the efficiency of DPSCs for sustainable solar energy conversion. When discussing the $V_{OC}$ of the device, the maximum value of 1.05 V is achieved with thickness of absorber layer 400 nm and that of an ETL is 600 nm. In contrast, minimum $V_{OC} = 0.948$V value occurs at the thickness of an absorber layer around 250 nm and that of an ETL at around 30 nm. These findings highlight the critical influence of absorber and ETL thicknesses on $V_{OC}$ in perovskite solar cells. When discussing the $J_{SC}$ of the device, the maximum value is 32 mA/cm² achieved with thickness of 1300 nm of an absorber layer and that of an ETL at around 600 nm. Conversely, minimum $J_{SC}$ value of 17.4 mA/cm² occurs at 100 nm thickness of an absorber layer and the thickness of an ETL at around 800 nm. These results underscore
the significant impact of absorber and ETL thicknesses on $J_{SC}$ in perovskite solar cells. When discussing the fill factor (FF) of the device, the maximum value of 76.2% is achieved with the thickness of an absorber layer at around 200 nm and that of an ETL at around 30 nm. In contrast, minimum FF value occurs around 54.6% with the thickness of absorber layer at 1300 nm and that of an ETL at 800 nm. These results highlight the significant impact of absorber and ETL thicknesses on FF in DPSC.
3.1.3 Effect of series resistance

The impact of series resistance ($R_S$) on DPSC performance (see Figure 6), with $R_S$ varying from 0 to 200 $\Omega \text{cm}^2$ and a fixed shunt resistance $R_{SH}$ of $10^5$ $\Omega \text{cm}^2$, was studied. All four parameters were analyzed by varying $R_S$. According to Fig. 6, $V_{OC}$ is not affected by varying $R_S$ from 0 to 200 $\Omega \text{cm}^2$. For $J_{SC}$, $R_S$ remained constant from 0 to 40 $\Omega \text{cm}^2$, then decreased exponentially up to 200 $\Omega \text{cm}^2$, as shown in Fig. 6. A dramatic reduction or exponential decay of FF and efficiency was observed in Fig. 6. Efficiency falls off rapidly as series resistance rises. The fill factor (FF) also exhibited a decreasing trend with the increment of $R_S$. However, $V_{OC}$ was not significantly affected. The PCE of this structure was influenced...
by the increment of $R_S$. The influence of $R_S$ on solar cell properties is clarified using (1).

$$I_{SC} = I_0 \left( e^{\frac{V_{oc}}{nKT}} - 1 \right)$$

$$I_{SC} = I_L - I_0 \left( e^{\frac{V_{oc}}{nKT}} - 1 \right) - \frac{V_{oc} + I_{SC}R_S}{R_{SH}}$$

Here $I_{SC}$ and $I_L$, respectively signify the short circuit current and light induced current. This formula states that when the value of $I_{SC}$ decreases, the value of $R_S$ increases. Most of the time, it is accountable for the decrease in PCE and FF[53][54].

\[\text{Figure 6. Effect of Series Resistance on cell performance}\]

3.1.4 Shunt resistance’s effect

Figure 7 illustrates the connection between PV parameters $V_{OC}$, $J_{SC}$, FF, and PCE and $R_{sh}$, which ranges from $10^1$ to $10^7 \ \Omega \ cm^2$ in ideal SC setups for a settled $R_S$. With the exemption of $J_{SC}$, $V_{OC}$, FF, and PCE values all take after the same slant when $R_{sh}$ rises. From $10^1 \ \Omega \ cm^2$ to $10^3 \ \Omega - cm^2$, PV performance indicators FF, PCE, and $V_{OC}$ increase rapidly and then saturate with further increases in $R_{sh}$. For $V_{OC}$, the FTO/WS$_2$/LNMO/Spiro/Au structure exhibits a maximum of $\sim 1.02$ V at $10^7$ and a minimum value of $\sim 0.31$ V at $R_{sh} = 10^1$. All specifications have nearly the same $J_{SC}$, with lowest and highest values of $\sim 29.5$ and $\sim 31$ mA/cm$^2$, respectively. The FF of the structure is highest at $\sim 63\%$ and lowest at $\sim 25\%$. With a maximum of $\sim 18.1\%$ and a minimum of $\sim 2.9\%$, an identical pattern is shown for
PCE. $R_{sh}$ is usually the result of defects incorporated into the PSCs during the production process. Junction current flow can be enabled at the p-n junction with very little resistance at a sufficiently large $R_{sh}$[55]. The pattern of variation in several PV parameters due to the change in $R_{sh}$ is consistent with a previous study [56].

![Figure 7. Effect of Shunt Resistance on cell performance](image)

### 3.1.5 Effect of temperature

Predicting how long SCs will last without experiencing appreciable PCE degradation requires an understanding of PV performance at high operating temperatures. Most SC design have layers that are prone to defects when they overheat, which results in variations in performance. Figure 8 illustrates how temperature variations affect the configuration’s performance criteria, such as $V_{OC}$, $J_{SC}$, FF, and PCE, for LNMO-based DPSCs. It is also important to note that the simulator under consideration does not currently handle temperature fluctuation with time. The primary limitation of the temperature model utilised in this study is that it only provides a broad summary of how temperatures affect DPSCs without accounting for temporal dimensions. The $V_{OC}$ values of all of the studied lead-free-based DPSCs decrease as the temperature rises and also result in an increase in reverse saturation current. The $V_{OC}$ of the FTO/WS$_2$/LNMO/Spiro-OMeTAD/Au DPSC decreased from 1.04 to 0.489 V. With increasing temperature, the short-circuit current density ($J_{SC}$) of the DPSCs remained relatively constant. The fill factor (FF) of the examined requirements dropped as the temperature
rose. However, there is negative impact on PCE due to an increment in temperature, resulting in decreased PCE for all of the devices.

![Graphs showing effect of temperature on cell performance.](image)

**Figure 8.** Effect of Temperature on cell performance

### 3.1.6 Effect of Total Defect Density of Absorber Layer

The performance and stability of the PSC are significantly affected by the total defect density of materials[57][58]. Add up to imperfection thickness of the fabric is subordinate on the quality of perovskite, CTL(Charge Transport Layer) and doping fabric utilized as well as on the fabrication/doping strategy utilized to manufacture the cell structure[59]. Bigger add up to deformity thickness of a fabric can lead to more noteworthy number of trap states and precious stone surrenders. Higher traps advance recombination and diminishes the development of charge carriers[60]. The lifetime of charge carrier is reduced with the increase of total defect density[61][62]. That is why we need the optimum thickness of the layer.

In our optimized PSC structure, the total defect density is increased from E13 to E18 cm$^{-3}$. It is evident from the Fig. 9 that at E18, higher is the trap which implies higher recombination. As a result, the solar cell’s parameters drop.

### 3.1.7 Effect of Interfacial Defect Density

At the two interfaces of perovskite layer with CTL, there is formation of two types of interfacial defects. One is HTL/Perovskite and the other one is Perovskite/ETL[63][64]. There
Effect of Total Defect Density of Absorber Layer on cell performance is increment in trap levels at the interface with the increase of such defects. This is the reason of increment of resistance in the cell, which has an impact on the flow of carriers that are charged. Thus, recombination increases and the performance of the cell decreases\cite{65}. The imperfection is shifted from E10 to E16 cm$^{-3}$ for both interfacing of the configuration, in order to analyze the effect of such defects. Fig. 10 and 11 is depicting the effect of the increase in the interface defect density on the performance of the solar cell. For both interfaces, the device showing degradation in the performance with the increase in defect density. For both interfaces, E10cm$^{-3}$ is chosen as the optimum inter facial defect density.
Figure 10. Effect of ETL/perovskite Defect Density on cell performance
3.1.8 Effect of capacitance

Figure 12 illustrates the impact of capacitance over a steady recurrence run of 1 MHz and a voltage range of $-0.8$ to $0.8$ V. Up to the saturation point, the capacitance grows exponentially with an increase in supply voltage. The specs show a tendency for the capacitance to increase with the voltage starting at about $-0.5$ V.
3.1.9 Effect of Current-Voltage Density and Quantum Efficiency

Fig. 13 depicts the current-voltage (JV) characteristics for the FTO/WS₂/La₂NiMnO₆/Spiro-OMeTAD/Au configuration. It can be seen that in this configuration the J_{SC} is 31 mA/cm². The quantum efficiency (QE) of novel device is in Fig. 14, in which QE versus wavelength is presented. Attaining 100% QE depicts that there is extreme absorption, thus causing a high creation of electron-hole pairs. Below wavelength of 380 nm, there is reflection in the front face which causes the loss shown in the QE figure. At higher wavelength >750 nm, there is recombination effect which causes sharp decline in quantum efficiency in the DPSC.

![Figure 13. Effect of Capacitance on cell performance](image)

![Figure 14. Quantum Efficiency and Current–Voltage Density](image)

3.2 Conclusion

The investigation into lead-free DPSCs has revealed promising results, with an achieved efficiency of 18.51%. The utilization of a novel device architecture involving WS₂ as the ETL and Spiro-OMeTAD as the HTL demonstrates the potential for enhancing DPSC performance. Firstly the device is optimized and then its series and shunt resistances have been
seen. Afterwards, the impact of temperature, total defect density of absorber layer and interfacial defect density is evaluated. The study identifies critical factors such as band alignment, layer thickness, and resistances that significantly impact DPSC efficiency. These findings contribute valuable insights into optimizing DPSCs for efficient solar energy conversion. Moving forward, further research focused on refining device architectures and understanding fundamental mechanisms will be crucial for advancing the practical application of DPSCs in renewable energy technologies.

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