

Simulation-Based Analysis of Environmentally Friendly Perovskite Solar Cells: Projecting 21.61% Efficiency with Lead-Free $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$

Ayush Jain, Poonam Subudhi, Gaurav Mani Khanal, and Deepak Punetha*

In this study, a simulation-based analysis of environmentally friendly, lead-free perovskite (PVK) solar cells (PSC) with high power conversion efficiency (PCE), is presented. Various PVK materials, including lead-, tin-, germanium-, and tin–germanium-based compounds, are evaluated through simulations to explore their impact on device performance. Among these, $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ demonstrates the highest simulated efficiency, with a rectangular cell architecture of 0.45×0.9 mm. Key parameters such as thickness, temperature, doping concentration, and bandgap are systematically varied in the simulations to study their effects on device performance. The optimized architecture is found to be Au/Spiro-MeOTAD (hole-transport layer)/ $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ /TiO₂ (electron-transport layer)/FTO, achieving a simulated PCE of 21.61%, with an open-circuit voltage (V_{oc}) of 1.2 V, short-circuit current density (J_{sc}) of 21.32 mA cm^{-2} , and fill factor of 84.43%. Furthermore, in this study, detailed electrical simulations (electric field distribution, Shockley–Read–Hall recombination, and electron and hole concentrations) and thermal simulations (nonradiative recombination heating, joule heating) of the device are included. In this work, the potential of lead-free PSCs is underscored and the importance of continuous simulation studies to design eco-friendly, high-efficiency photovoltaic devices is highlighted.

(PVK)-structured hybrid halide compounds. These compounds, known for their organo-mineral PVK structure, have revolutionized solar cell production by offering substantial advantages over conventional silicon-based cells, including high efficiency and lower production costs.^[1,2] The materials with the chemical structure ABX_3 , where “A” can be an organic or inorganic cation, “B” an inorganic cation, and “X” an inorganic anion or polyanion is referred to as a “perovskite” and shown in **Figure 1**. These materials exhibit exceptional properties such as high absorption coefficients, tunable bandgaps, and long charge carrier diffusion lengths, making them highly suitable for solar cell applications.^[3–5]

PVK photovoltaic (PV) cells have quickly surpassed expectations in terms of performance. Achieving impressive power conversion efficiencies (PCEs) of up to 25.2%, and sometimes even higher, within a short period, these cells have demonstrated their potential to redefine the solar energy landscape.^[6–8] However, the wide-

spread adoption of lead-based PVK cells has been hindered by serious environmental and health concerns due to the toxicity of lead. This has prompted intensive research into lead-free alternatives that can maintain the high efficiency and cost-effectiveness of traditional PVK cells while mitigating these risks.^[9] To counter the toxic effects of Pb several nontoxic elements like Bi, Ge, Ag, and Sn are being studied. Replacements like Sn and Ge are being extensively studied as they solve the problem of moisture and toxicity. The tendency of Ge^{2+} to lose an unpaired electron result in its chemical instability.^[10] From the same group, the optical bandgap of the Sn-based absorption results in the range of 1.2 to 1.4 eV. In general, to increase the stability of tin (Sn), Sn halide additives (SnX_2 ; X = Cl, Br,) are used.^[11–13] Also, using formamidinium (FA) instead of methylammonium (MA) has the potential to solve the problem of moisture instability. Furthermore, the addition of inorganic cation cesium (Cs) along with MA and FA in the PVK can improve the instability issue. Halide-based PVK materials are used as they have the appropriate bandgap in the range of 1.25–1.75 eV.^[14,15] A PVK-based solar cell (PSC) comprises multiple layers like FTO, electron-transport layer (ETL), absorber layer, hole-transport layer (HTL), and the back contact (Au). By choosing the appropriate electron-transport material (ETM) and

1. Introduction

Solar energy is one of the most promising renewable energy sources to meet the escalating global demand for energy. Over the years, significant advancements have been made in solar cell technology, particularly with the advent of perovskite

A. Jain, G. M. Khanal
Department of Electronics Engineering
JK Lakshmi Pat University
Jaipur 302026, India

P. Subudhi
School of Advanced Sciences
Vellore Institute of Technology
Chennai 600127, India

D. Punetha
Department of Electronics and Communication Engineering
Motilal Nehru National Institute of Technology Allahabad
Prayagraj, Uttar Pradesh 211004, India
E-mail: deepakpunetha@mnnit.ac.in

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/pssa.202400727>.

DOI: 10.1002/pssa.202400727

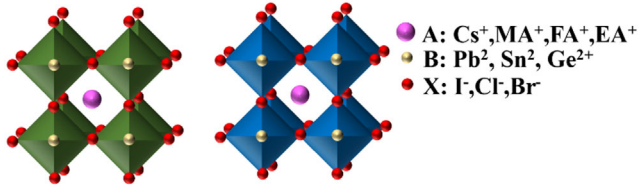


Figure 1. Schematic of 3D perovskite structure.

hole-transfer material (HTM) materials and varying their combinations, the PVK layer's efficiency is increased. Such pairings have the potential to create solar cell technology that is extremely efficient for future generations.^[16,17] The main functions of the ETL are to collect electrons from the PVK absorber layer and move them to the anode and to restrict the hole in the layer. Chemical stability is essential for a perfect ETL to avoid a chemical interaction with the absorber layer. Within the field of modern research, ZnO and TiO₂ are often used as effective ETL. The HTL gathers holes from the PVK layer and transfers them to the cathode, thereby limiting electrons. The HTL layer should be hydrophobic since it comes into direct contact with moisture and the objective is to shield the absorber layer from moisture.^[18,19] Maximum efficiency can be achieved by employing TiO₂ as an ETL. Mostly TiO₂ is utilized in solar cells in its high-temperature phase or rutile phase; nevertheless, the utilization of such high-temperature grown TiO₂ as ETL in PSC is limited.^[20,21] Similarly, HTLs like PEDOT:PSS and Spiro-MeOTAD are sometimes appropriate because of their stability and cost-effectiveness. Furthermore, a few research on the optimization of HTL and ETL have previously been published.^[22,23] It is also possible to increase the performance of the PSCs by varying parameters like thickness, operating temperature, bandgap, doping concentration, defect density, etc.

This article focuses on the simulation of single lead-free PVK cells. These cells are configured with Spiro-MeOTAD as the HTM and TiO₂ as the ETM, aiming to offer viable solutions to the issues associated with lead-based solar cells. The study specifically examines PVK materials containing elements such as tin or germanium, or combinations thereof, which are simulated to assess their potential to deliver comparable performance without environmental drawbacks. The research includes a detailed analysis of simulation techniques and the materials used. In particular, the study investigates the impact of varying the thickness, temperature, etc., of the PVK layer on key solar parameters such as efficiency and fill factor (FF). By exploring 16 different PVK materials with variations in the "A" component (including MA, FA, Cs, and ethyl-ammonium [EA]), as well as alternatives for "B" (including lead [Pb²⁺], tin [Sn²⁺], and germanium [Ge²⁺]), and "X" (primarily iodine [I]), the article provides a comparative evaluation of their performance characteristics. This research aims to contribute to the development of lead-free PVK solar cells that not only match but potentially surpass the efficiency and cost-effectiveness of traditional lead-based cells while addressing critical environmental and health concerns associated with lead toxicity. These advancements are crucial for accelerating the widespread adoption of PVK solar technology and achieving sustainable energy solutions on a global scale.

2. Device Architecture and Simulation

The parameters of various PSCs were studied before designing the actual solar device. Using the COMSOL software, the PVK's cell electrical and physical properties were modeled for the simulation. COMSOL Multiphysics is designed for use in a variety of engineering and physics applications, like coupled phenomena and Multiphysics. COMSOL Multiphysics offers an IDE and a unified workflow for applications in electrical, mechanical, fluid, acoustics, and chemistry.^[24]

A planar device structure made up of back contact (Au), HTL layer (Spiro-MeOTAD), PVK material, ETL (TiO₂) layer, and FTO was simulated (**Figure 2**). The absorber layer was composed of (Cs,MA,FA,EA)PbI₃, (Cs,MA,FA,EA)SnI₃, (Cs,MA,FA,EA)GeI₃, and (Cs,MA,FA,EA)Sn_{0.5}Ge_{0.5}I₃. To create a high-efficiency solar cell, these ETL and HTL materials were selected because of their appropriate band edges, which match the valence band maximum and conduction band minimum of the absorber materials. Using these parameters, a generation rate was defined and governed by these equations

$$\nabla \cdot J_n + = -qR_n, \nabla \cdot J_p + = qR_p \quad (1)$$

$$R_n = -G_{n,0} \quad (2)$$

$$R_p = -G_{p,0} \quad (3)$$

The remaining simulation variables are left at their normal settings, and the operating temperature is set at 298.15 K. The Shockley–Read–Hall (SRH) model was used as a trapping model governed by these equations

$$p_1 = \gamma_p n_{i,eff} \exp\left(-\frac{\Delta E_t}{k_B T}\right) n_1 = \gamma_n n_{i,eff} \exp\left(\frac{\Delta E_t}{k_B T}\right) \quad (4)$$

$$n_{i,eff} = \sqrt{N_{c0} N_{v0}} \exp\left(-\frac{E_g - \Delta E_g}{2k_B T}\right) \Delta E_t = E_t - E_i \quad (5)$$

$$R_n = \frac{np - \gamma_n \gamma_p n_{i,eff}^2}{\tau_p(n + n_1) + \tau_n(p + p_1)} = R_p \quad (6)$$

$$\nabla \cdot J_n + = -qR_n, \nabla \cdot J_p + = qR_p \quad (7)$$

Poisson's equation and the continuity charge carrier equations are used to simulate PV devices.^[25] The prime parameters of devices such as V_{oc} , J_{sc} , PCE, and FF are estimated from the simulation. Poisson's equation of the semiconductor devices, which describe the relationship between the electric field of a p–n junction (E) and the space charge density (p), is described as

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{\partial E}{\partial x} = -\frac{\rho}{\epsilon_s} = -\frac{q}{\epsilon_s} [p - n + N_D^+(x) - N_A^-(x) \pm N_{def}(x)] \quad (8)$$

ψ : the electrostatic potential, p (n): the hole (electron) density, q : elementary charge, $N_A^-(N_D^+)$: density of ionized acceptors (donors), ϵ_s : static relative permittivity of the medium, N_{def} : defect density (Donor or acceptor).

The continuity equations for electrons and holes in a steady state are given as

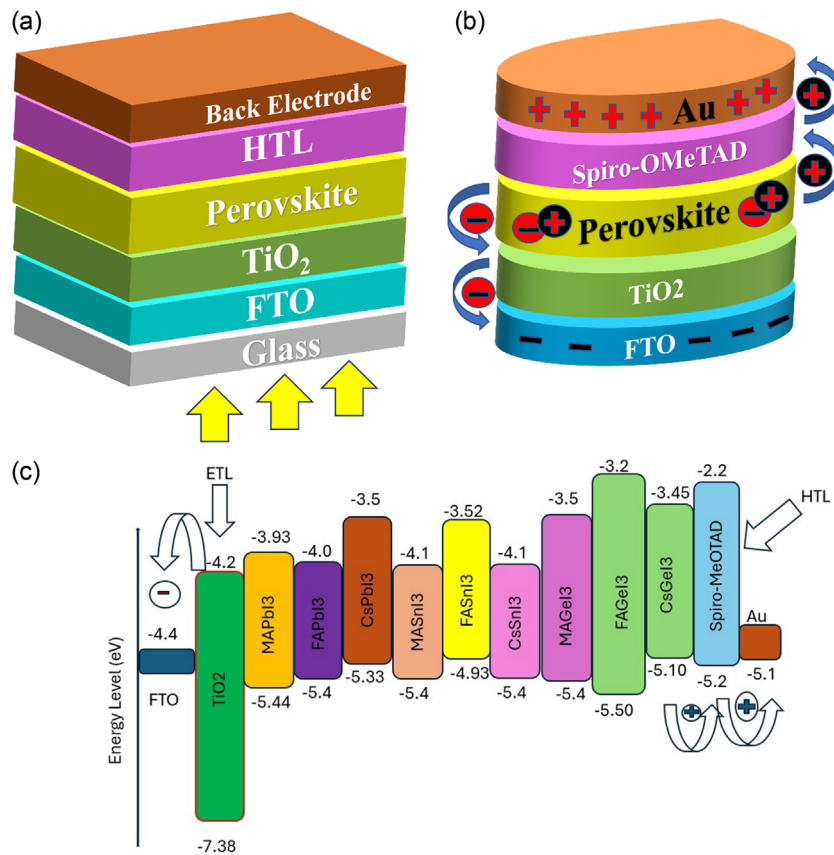


Figure 2. a) Device structure, b) charge carriers schematic representation, c) schematic representation of the transformation of the charge carriers with simplified flat band energy level diagram of PSC.

$$-\frac{\partial j_n}{\partial x} - U_n + G = \frac{\partial n}{\partial t} \quad (9)$$

$$-\frac{\partial j_p}{\partial x} - U_p + G = \frac{\partial p}{\partial t} \quad (10)$$

j_n, j_p : electron and hole current densities, $U_{n,p}$: net recombination rates, and G : electron–hole generation rate.

The electron and hole current density are given by

$$J_n = -\frac{\mu_n n}{q} \frac{\partial E_{F_n}}{\partial x} \quad (11)$$

$$J_p = +\frac{\mu_p p}{q} \frac{\partial E_{F_p}}{\partial x} \quad (12)$$

$\mu_{n(p)}$: electron (hole) mobility; q : elementary charge.

3. Results and Discussion

In the current study, 16 different combinations of PSCs have been simulated using the COMSOL 6.2 Multiphysics. Every simulation has been done by making a constant ETL layer (TiO₂) and HTL layer (Spiro-MeOTAD). The movement of electron and hole charge carriers in PVK solar cells, as well as FFs, has been significantly impacted by ETL and HTL. The ETL is primarily

responsible for limiting the hole in the layer, collecting electrons from the PVK absorber layer, and transferring them to the anode. An ideal ETL must have chemical stability to prevent a chemical reaction with the absorber layer. In the sphere of contemporary research, ZnO and TiO₂ are frequently employed as efficient ETL. Electrons are constrained by the HTL, which also gathers holes from the PVK layer and transports them to the cathode. Since the HTL layer comes into direct contact with moisture and protecting the absorber layer from moisture is our goal, the HTL layer should have a hydrophobic character.

3.1. Variation of Shape and Dimension of Solar Cell Device

By modeling each of the examined device structures with the associated device parameters as given in Table 1–5, the performance parameters are calculated. As observed in Figure 3, higher PCE is obtained for device structure CsSn_{0.5}Ge_{0.5}I₃ and EAPbI₃. Also, these materials provide a high-value FF. Despite that CsSn_{0.5}Ge_{0.5}I₃ has smaller bandgap of 1.5 eV allowing broader absorption, its lower short-circuit current density (J_{sc}) results from higher carrier recombination and suboptimal energy alignment with ETL/HTL layers. These factors reduce charge extraction efficiency. Since this article's focus is on Pb-free solar cells, we will continue to explore the properties and ways to increase the efficiency of CsSn_{0.5}Ge_{0.5}I₃. However, it is also important to

Table 1. Parameters of lead-based perovskites.

Material property	CsPbI ₃ ^[36]	MAPbI ₃ ^[37]	FAPbI ₃ ^[38]	EAPbI ₃ ^[39]
Thickness [nm]	350	350	350	350
Bandgap E_g [eV]	1.694	1.55	1.51	1.93
Electron affinity X [eV]	3.95	3.9	4	3.78
Dielectric permittivity	6	30	6.6	8.2
CB density of state [cm ⁻³]	1.1×10^{20}	2×10^{18}	1.2×10^{18}	1×10^{18}
VB density of state [cm ⁻³]	8×10^{19}	2×10^{18}	2.9×10^{18}	1×10^{18}
Electron mobility (μ_n) [cm ² V ⁻¹ s ⁻¹]	25	10	2.7	22
Hole mobility (μ_p) [cm ² V ⁻¹ s ⁻¹]	25	10	1.8	22
Acceptor density NA [cm ⁻³]	–	1×10^{17}	1.3×10^{16}	7×10^{16}
Donor density ND [cm ⁻³]	1×10^{15}	–	1.3×10^{16}	–

Table 2. Parameter of tin-based perovskites.

Material property	CsSnI ₃ ^[40]	MASnI ₃ ^[41]	FASnI ₃ ^[42]	EASnI ₃ ^[43]
Thickness [nm]	350	350	350	350
Bandgap E_g [eV]	1.27	1.3	1.4	1.17
Electron affinity X [eV]	4.47	4.17	3.9	3.85
Dielectric permittivity	18	8.2	6	8.4
CB density of state [cm ⁻³]	1×10^{19}	1×10^{18}	1×10^{18}	1×10^{18}
VB density of state [cm ⁻³]	1×10^{19}	1×10^{18}	1×10^{18}	1×10^{18}
Electron mobility (μ_n) [cm ² V ⁻¹ s ⁻¹]	4.37	1.6	22	25
Hole mobility (μ_p) [cm ² V ⁻¹ s ⁻¹]	4.37	1.6	22	25
Acceptor density NA [cm ⁻³]	1.8×10^{16}	1×10^{14}	7×10^{16}	6×10^{16}
Donor density ND [cm ⁻³]	–	–	–	–

Table 3. Parameter of germanium-based perovskites.

Material property	CsGeI ₃ ^[44]	MAGeI ₃ ^[45]	FAGeI ₃ ^[46]	EAGeI ₃ ^[47]
Thickness [nm]	350	350	350	350
Bandgap E_g [eV]	1.6	1.9	2.2	1.3
Electron affinity X [eV]	3.523	3.98	3.52	3.9
Dielectric permittivity	18	10	18	8.2
CB density of state [cm ⁻³]	1×10^{18}	1×10^{16}	1×10^{18}	1×10^{19}
VB density of state [cm ⁻³]	1×10^{19}	1×10^{15}	1×10^{19}	1×10^{18}
Electron mobility (μ_n) [cm ² V ⁻¹ s ⁻¹]	20	16.2	20	22
Hole mobility (μ_p) [cm ² V ⁻¹ s ⁻¹]	20	10.1	20	22
Acceptor density NA [cm ⁻³]	2×10^{16}	1×10^9	2×10^{18}	7×10^{15}
Donor density ND [cm ⁻³]	–	1×10^9	–	–

determine the shape of the solar cell which gives the best performance. Hence, parameters like temperature, thickness, bandgap, and doping concentration of solar cell are varied by keeping their area constant and changing the shape from rectangle to square to cylinder.

Table 4. Parameter of tin–germanium-based perovskites.^[48,49]

Material property	CsSn _{0.5} Ge _{0.5} I ₃	MASn _{0.5} Ge _{0.5} I ₃	FASn _{0.5} Ge _{0.5} I ₃	EASn _{0.5} Ge _{0.5} I ₃
Thickness [nm]	350	350	350	350
Bandgap E_g [eV]	1.5	1.192	1.8	1.235
Electron affinity X [eV]	3.9	4.2	3.9	3.78
Dielectric permittivity	28	30	8.2	7.8
CB density of state [cm ⁻³]	3.1×10^{19}	2×10^{19}	1×10^{18}	1×10^{19}
VB density of state [cm ⁻³]	3.1×10^{18}	2×10^{19}	1×10^{18}	2.5×10^{18}
Electron mobility (μ_n) [cm ² V ⁻¹ s ⁻¹]	213	300	22	20
Hole mobility (μ_p) [cm ² V ⁻¹ s ⁻¹]	100	300	22	20
Acceptor density NA [cm ⁻³]	1×10^{19}	1×10^{17}	7×10^{16}	6.5×10^{15}
Donor density ND [cm ⁻³]	–	–	–	–

Table 5. Parameter of ETL, HTL, and FTO.^[50]

Material property	TiO ₂	Spiro-MeOTAD	FTO
Thickness [nm]	100	100	100
Bandgap E_g [eV]	3.2	3	3.5
Electron affinity X [eV]	4.26	2.45	4
Dielectric permittivity	100	3	9
CB density of state [cm ⁻³]	2×10^{18}	1×10^{19}	2.2×10^{18}
VB density of state [cm ⁻³]	1.8×10^{19}	1×10^{19}	1.8×10^{19}
Electron mobility (μ_n) [cm ² V ⁻¹ s ⁻¹]	2×10^4	50	20
Hole mobility (μ_p) [cm ² V ⁻¹ s ⁻¹]	1×10^3	50	10
Acceptor density NA [cm ⁻³]	–	1×10^{17}	0
Donor density ND [cm ⁻³]	6×10^{19}	–	1×10^{19}

As evident from the graphs, PCE have high values while the shape of the cell is a rectangle. Therefore, the rest of the simulations are carried out by taking rectangular solar cell. It is also necessary to figure out the optimized dimension for a solar cell. This is done by changing the area of the cell by changing its width and depth but keeping the height constant. As can be observed from **Figure 4**, solar cells with varying width and depth are depicted with changing parameters in temperature, thickness, etc. It is evident from the graph that the solar cell has high value of PCE when the width and depth is $0.45 \times 0.9 \text{ mm}^2$. Hence, the simulations provided later are done by taking these dimensions into consideration.

As can be observed from **Figure 5**, solar cells with varying width and depth are depicted with changing parameters in temperature, thickness, etc. It is evident from the graph that

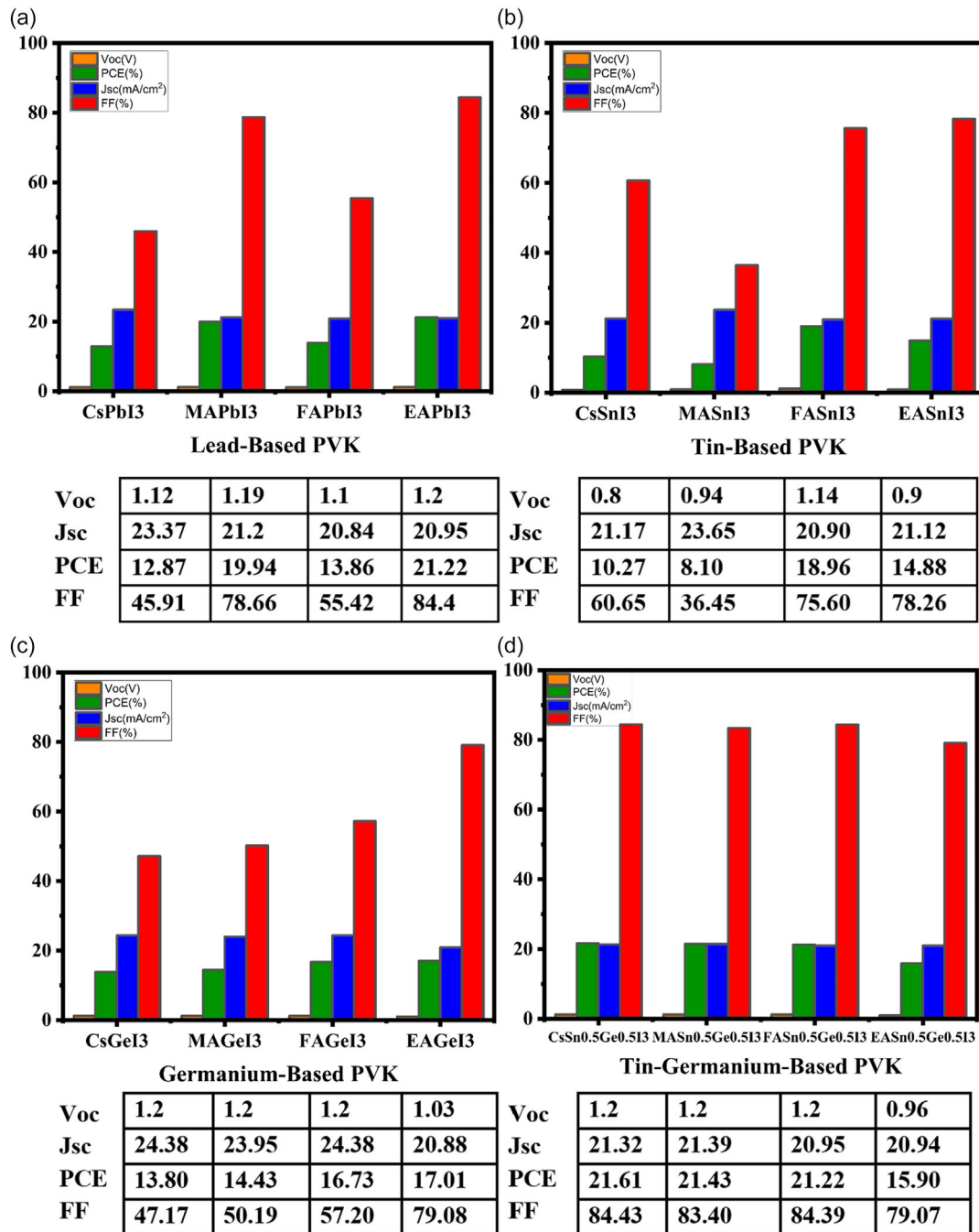


Figure 3. Parameters of different cells: a) lead-based PSC, b) tin-based PSC, c) germanium-based PSC, and d) tin-germanium-based PSC.

the solar cell has high value of PCE when the width and depth is $0.45 \times 0.9 \text{ mm}^2$. Hence, the simulations provided later are done by taking these dimensions into consideration. PV device parameters are further influenced by basic parameters such as doping concentration, thickness of the PVK material, bandgap (E_g), operating temperature (T), and so on. To find the ideal device configuration that offers the highest level of efficiency, these parameters are therefore methodically changed in **Figure 6**.

3.2. Effect of Temperature on the Performance of PSC

As seen in **Figure 6a**, the temperatures have been changed from 280 to 380 K to examine the change in performance parameters. The chart shows that while J_{sc} is relatively constant with very minor changes with rising temperatures, V_{oc} , FF, and PCE are decreasing. The reasons for this degradation of PCE are as follows: 1) the temperature-dependent concentration and mobility of the carriers create an obstruction in the transport path; 2) an

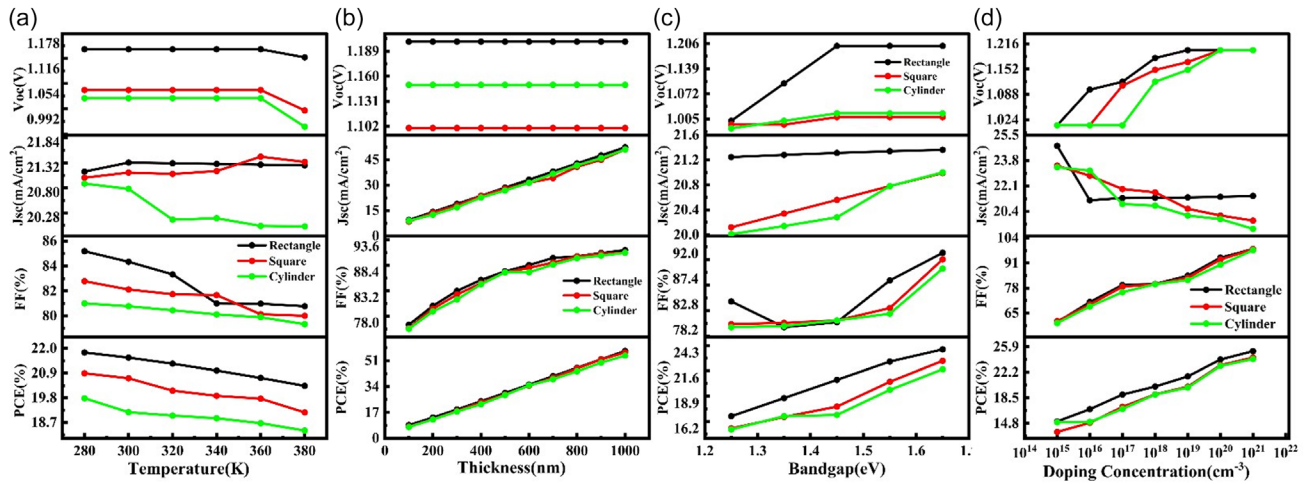


Figure 4. Variation on solar cell parameters by changing a) temperature, b) thickness, c) bandgap, and d) doping concentration for different shapes.

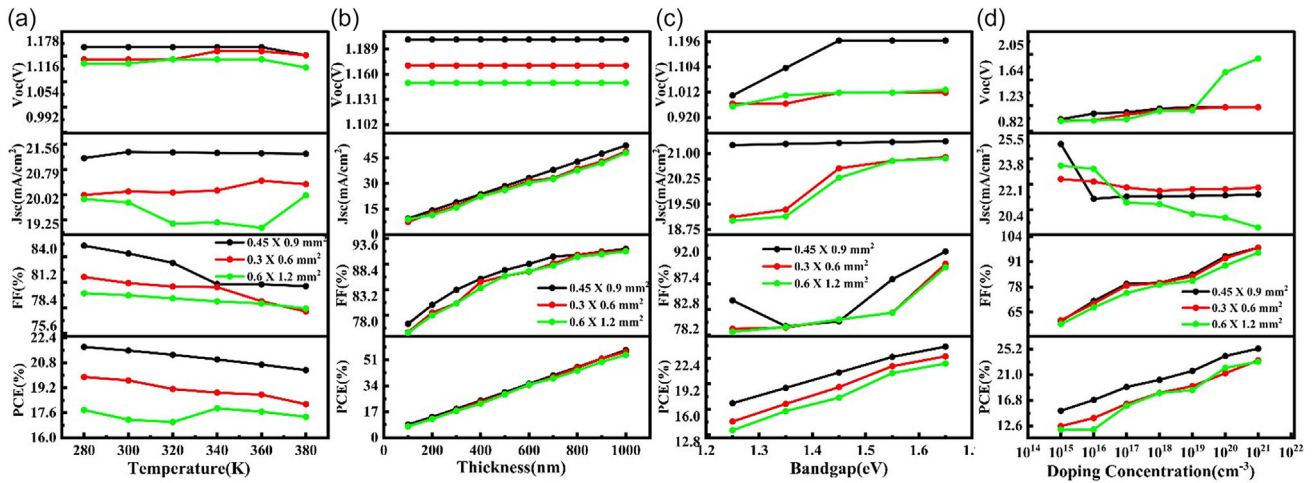


Figure 5. Variation on solar cell parameters by changing a) temperature, b) thickness, c) bandgap, and d) doping concentration for different dimensions.

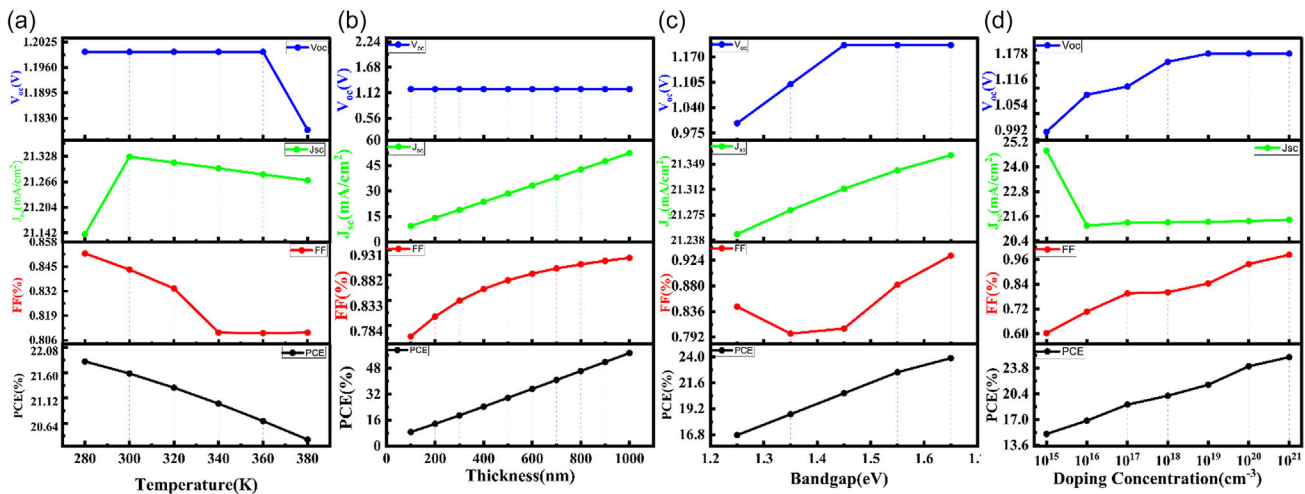


Figure 6. Variation of a) temperature, b) thickness, c) bandgap, and d) doping concentration of perovskite absorbing material.

increase in temperature also increases the defect density within the layers;^[26,27] and 3) the deformation and distortion also cause an increase in stress and strain.^[28] So, the optimum operating temperature as can be observed from the graph is 300 K.

3.3. Effect of the PVK Layer Thickness

The PSC light-absorbing substance is especially important, and achieving high efficiency depends on its thickness. It is observed in Figure 6b that thorough analysis of the effects of PVK layer thickness variation on PV solar cells has been conducted within the 100–1000 nm range for an ideal thickness of the PVK. In this work, a considerable number of photons are absorbed, increasing the thickness of the solar cell absorber layer and, consequently, the PCE, which in turn produces a vast number of generations of electron and hole pairs. Additionally, as the layer thickness increases, the possibility of simultaneous recombination increases.^[29] It is discovered that the absorber layer's ideal thickness is around 600 nm.

3.4. Effect of the Bandgap of the PVK Material

According to the Shockley–Queisser efficiency limit, the bandgap of the absorber layer must be as close to 1.34 eV as possible for PV devices to function at their best. The PVK absorber layer bandgap changed in the simulation from 1.25 to 1.65 eV. From Figure 6c it can be observed, as bandgap values increase, all other metrics (J_{sc} , V_{oc} , and PCE) increase while the FF initially decreases. The creation of charge carriers and subsequent exciton separation cause the absorber layer bandgap to grow, which in turn causes an increase in (V_{oc}). Furthermore, the disparity

between the absorber layer and HTL lowers the FF to a certain point.^[30]

3.5. Effect of Doping Concentration of the PVK Material

The kind and amount of doping are crucial factors in enhancing the efficiency of PVK solar cells. A shallow point defect can give rise to unwanted doping in the absorbing substance. In this work, the doping concentration of the PVK material is adjusted between 10^{15} and 10^{21} cm^{-3} as shown in Figure 6d to investigate the impact of different doping concentrations on the solar cell primary characteristics. The doping concentration in PVK material is enhanced, which raises the electric field inside the absorber layer and improves exciton segregation. This could lead to an improvement in solar cell device performance.^[31] The doping concentration of 10^{15} is found to be the optimum for the performance of the solar cell after which the value of J_{sc} decreases.

3.6. Electrical Simulation

The formation and manipulation of the depletion region and its associated electric field are pivotal in solar cell design. Understanding and optimizing these factors are essential for achieving higher efficiencies and improving the overall performance of PV devices. It can be observed in Figure 7a that at 600 nm the values of electric field and SRH recombination are 10^7 and 10^{30} . In solar cell technology, the interface between materials with different doping levels creates a p–n junction, leading to the formation of a depletion region. This region is characterized by a lack of free charge carriers due to the

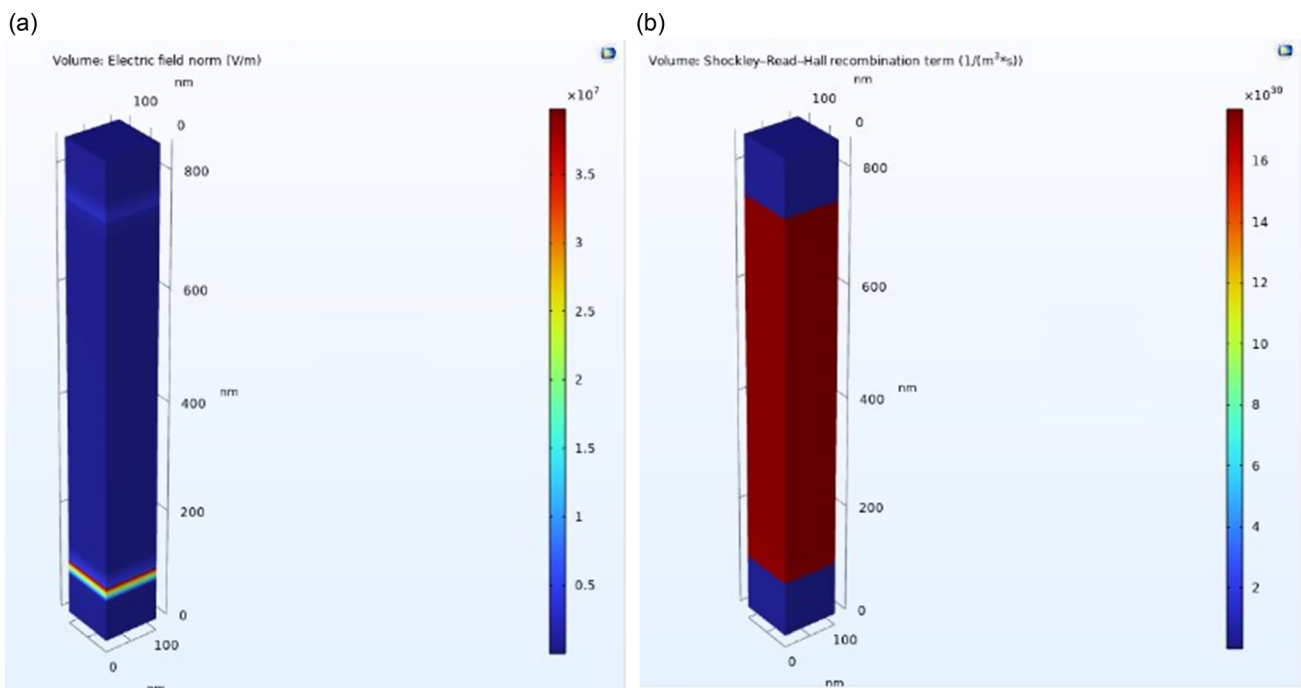


Figure 7. a) Electric field distribution and b) SRH recombination profile.

diffusion of the majority of carriers across the junction. The electric field within this depletion zone is crucial for the separation of photogenerated electron–hole pairs (excitons) produced by incident photons. This separation is essential for generating an electrical current in the solar cell.^[32] The dynamics of carriers within the depletion region are governed by the Poisson equation^[33]

$$\nabla \cdot (\nabla \Phi) = -\frac{\rho}{\epsilon_0 \epsilon_r} \quad (13)$$

which describes the electric potential distribution, and the current continuity equation, which ensures the conservation of charge. These equations quantify how the electric field influences carrier movement and recombination.

Efficient carrier separation is vital to prevent electron–hole pairs from recombining before contributing to the electrical output. The width of the depletion region plays a critical role here; a narrower depletion region allows for faster separation of carriers and reduces recombination rates. Consequently, this extends the lifetimes of carriers within the solar cell, thereby enhancing its overall performance.^[34] One significant aspect influencing carrier recombination in the depletion region is SRH recombination. This non-radiative process occurs through defects or traps within the material (Figure 7b). The electric field gradient within the narrow depletion region can affect the likelihood of carriers encountering these traps, thereby influencing the recombination rate. Engineers focus on minimizing defects and optimizing the electric field distribution to maximize carrier collection efficiency.

3.7. Carrier Concentration Simulation

In solar cell technology, the distribution of electron (n) and hole (h) concentrations across different layers plays a critical role in determining the device efficiency. The electron concentration profile typically shows its highest value in the FTO layer, which functions as the ETL. In **Figure 8a**, high value of electron concentration is observed at 600 nm (10^{24}). This layer facilitates the efficient collection and transport of electrons generated within the PVK absorber layer. The high electron concentration in FTO indicates effective extraction and transport mechanisms, crucial for minimizing losses and maximizing current generation in the solar cell.

Conversely, the hole concentration (h) exhibits an inverse profile compared to electrons. It is lowest in the FTO layer and highest in the Spiro-OMeTAD layer, known as the HTL. Spiro-OMeTAD is responsible for collecting and transporting holes from the PVK layer to the electrode. In **Figure 8b**, high value of electron concentration is observed at 600 nm (10^{24}). The significant concentration of holes in Spiro-OMeTAD signifies effective hole collection and transport, essential for completing the electrical circuit and achieving high current output in the solar cell. Photogenerated carrier distribution within the solar cell structure is concentrated near the p–n junction or within the depletion width of the PVK absorber layer. This region experiences the highest concentration of both electrons and holes due to the strong electric field that facilitates the efficient separation of electron–hole pairs.^[35] Optimizing the distribution of electron and hole concentrations is crucial for enhancing solar cell

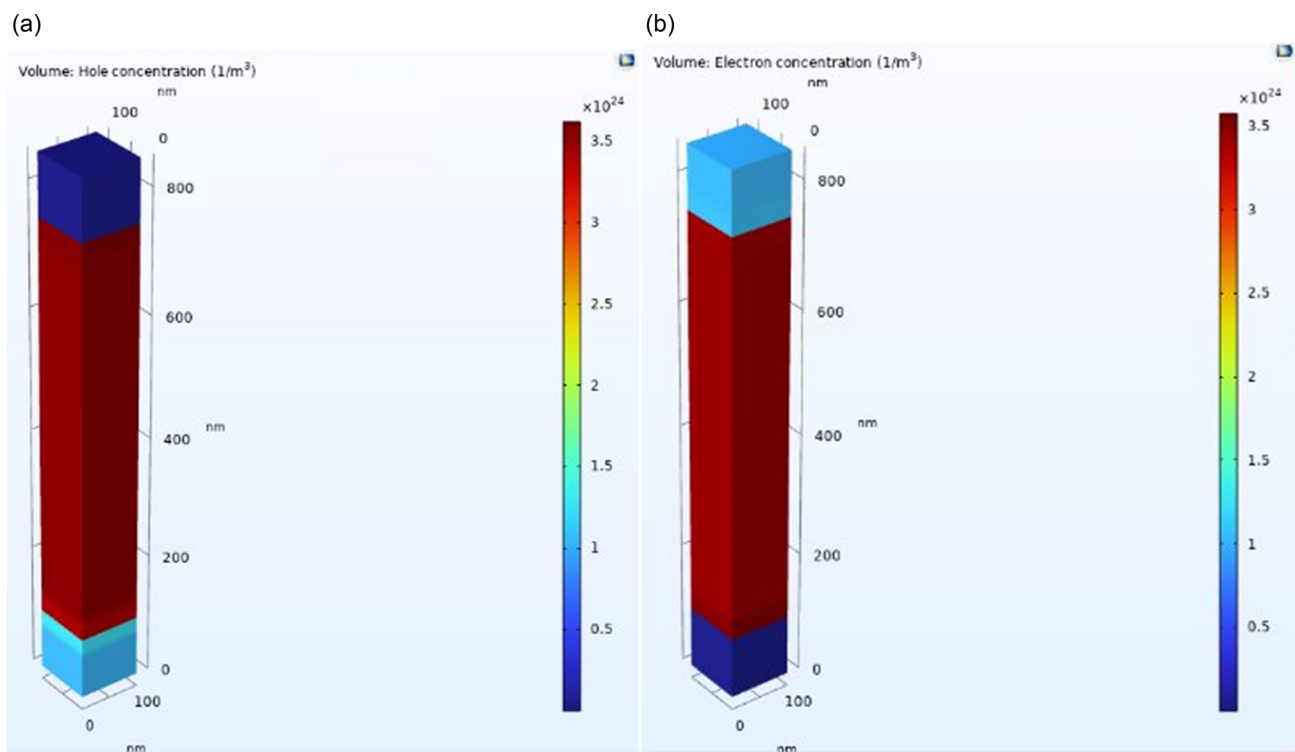


Figure 8. a) Hole concentration and b) electron concentration.

performance. Efficient extraction and transport of charge carriers minimize losses due to recombination, thereby boosting the PV conversion efficiency. The profiles observed in experimental figures underscore the strategic design and function of each layer—FTO for electron transport and Spiro-OMeTAD for hole transport—in achieving optimal charge carrier collection and current generation.

3.8. Thermal Simulation

Efficient management of heat within the solar cell is crucial for maintaining its performance and longevity. Excessive heating can increase nonradiative losses and potentially alter material properties, reducing overall efficiency. Temperature distribution in thin-film solar cells remains relatively uniform across their structure due to their low thermal mass and rapid heat dissipation characteristics. These cells are designed to minimize temperature gradients under normal operating conditions, ensuring consistent performance throughout. For the steady-state conduction with internal heat generation, the differential equation describes the temperature profile within the cell

$$-k\nabla^2 T + Q = \rho_p C_p \frac{dT}{dt} \quad (14)$$

When electrons and holes recombine without emitting photons, particularly near the depletion region it gives rise to nonradiative recombination heat. This region experiences heightened recombination rates due to the strong electric field, resulting in localized heat generation.^[33] The heat generated from the SRH recombination processes is a function of the energy bandgap (E_g), thermal energy (kT), and the SRH

recombination coefficient (U_{SRH}). In this article, the value of nonradiative recombination heat is found to be 10^{12} at 600 nm and shown in **Figure 9**.

$$H_{SRH} = (E_g + 3kT) \cdot U_{SRH} \quad (15)$$

Joule heating, in contrast, occurs due to resistive losses as electric current flows through materials with resistance. In solar cells, Joule heating predominantly occurs in the depletion region near the p–n junction. The electric field in this region accelerates the movement of photogenerated carriers, causing collisions and resistive losses that manifest as heat. Joule heat generation is proportional to the product of the electric field strength ϵ and the local current density (J). The value of Joule heating is close to zero at 600 nm

$$H_{joule} = J \cdot E \quad (16)$$

Both nonradiative recombination heat and Joule heat exhibit comparable magnitudes, typically ranging from 10^{12} to 10^{15} W m^{-3} , in their respective regions of intensity. Nonradiative recombination heat is concentrated near the p–n junction, influenced by the rate of carrier recombination, while Joule heat is distributed along the path of current conduction, with higher levels near electrodes like TiO_2 and FTO layers due to higher current densities.

3.9. Electric Potential and Bands

Figure 10a shows the change in energy potential concerning arc length (nm). The HTL side has higher potential because it collects positive charge carriers (holes) with higher mobility in

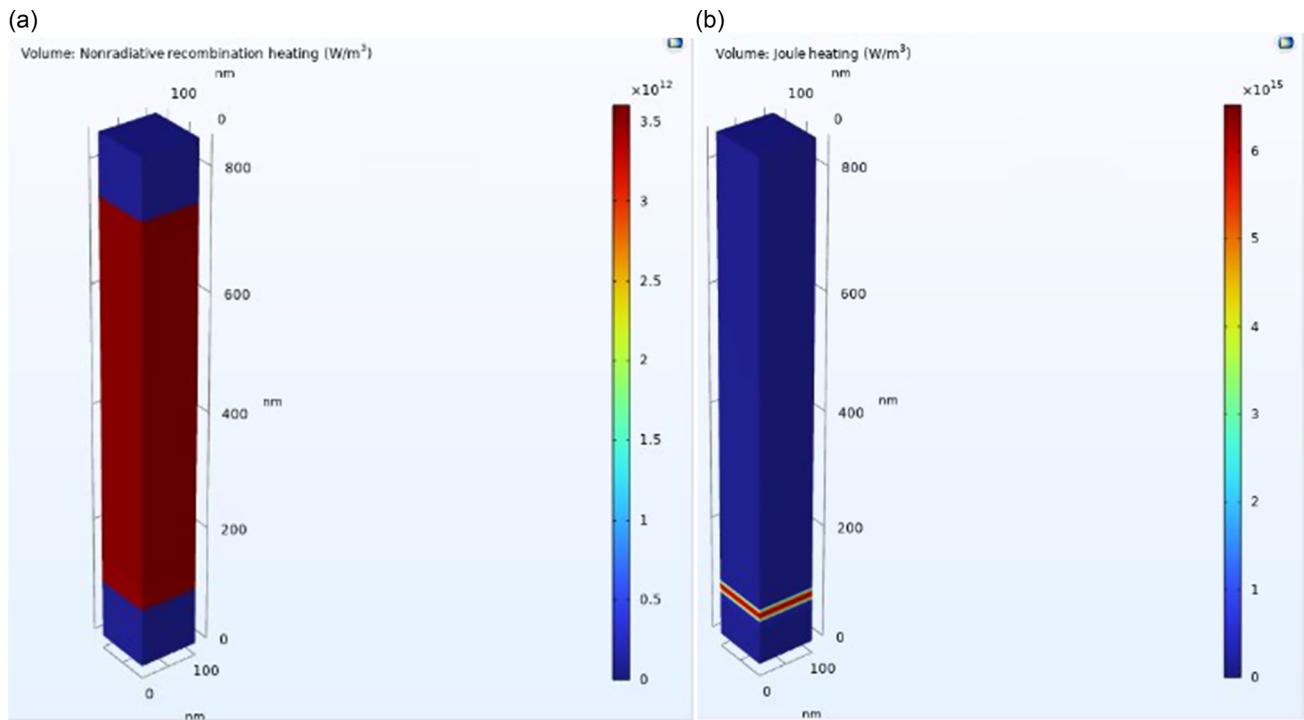


Figure 9. a) Non-radiative recombination heating and b) Joule heating.

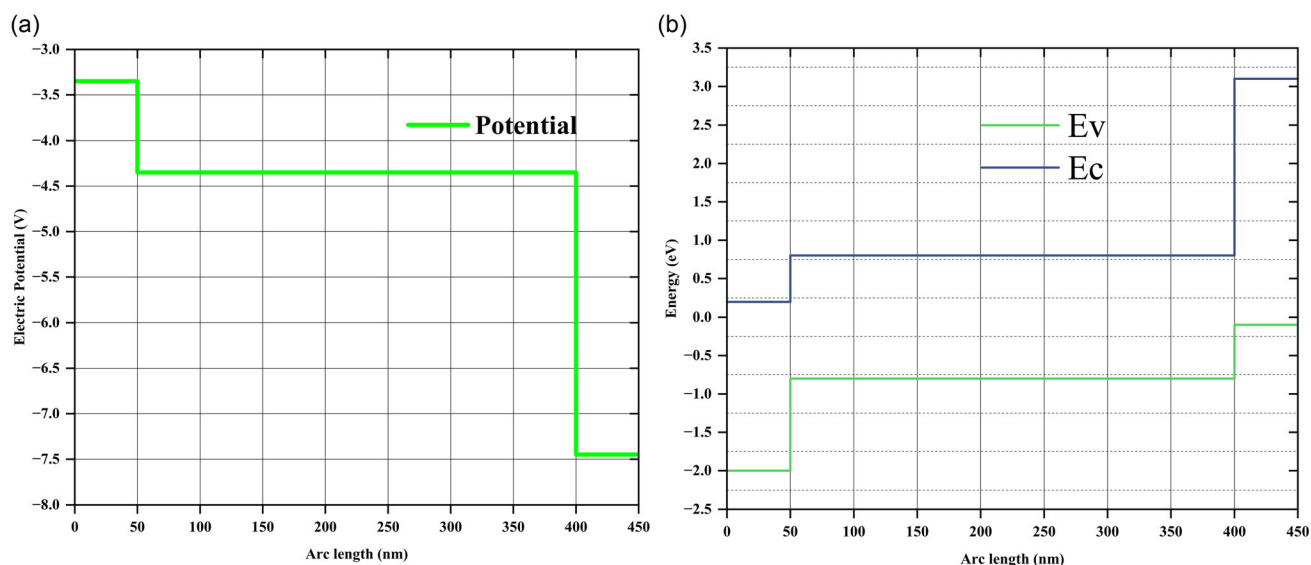


Figure 10. a) Electric potential and b) energy bands.

HTL while ETL collects electrons with higher mobility in ETL. Thus, an electric field is generated due to charge separation, and the necessary potential gradient for efficient collection and extraction of electrical energy generated by the solar cell is established. In Figure 10b, the energy of conduction and valence band is shown with the energy of the conduction band higher than the valence band as expected in any semiconductor material because it represents the energy required to free electrons from their bound states in the valence band, allowing them to move and conduct electricity within the material.

3.10. Comparative Study of Experimental and Simulated $J-V$ Characteristics

The most important factor in solar cells is the analysis of a combination of current density and voltage. Both the experimented and simulated $J-V$ curves are depicted in Figure 11. In the

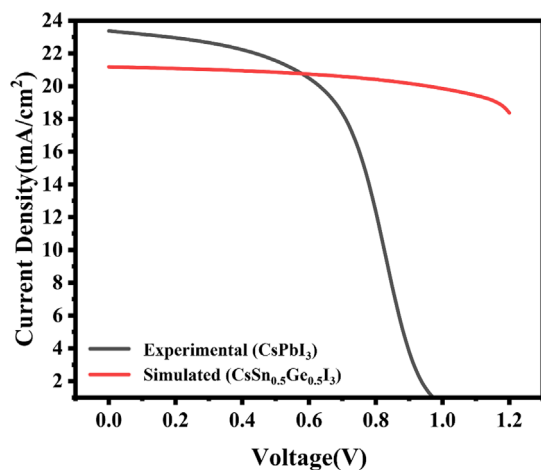


Figure 11. Comparative $J-V$ plot for experimental and simulated devices.

Table 6. Comparative summary of device parameters with reported results of PSC.

V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	References
1.14	20.9	75.6	18.96	This work
1.2	20.95	84.4	21.22	This work
1.2	21.39	83.4	21.43	This work
1.2	21.32	84.43	21.61	This work
0.89	22.79	65.28	13.35	[12]
1.34	15.55	82.73	18.01	[31]
1.176	12.67	84.59	12.61	[25]
0.849	20.89	83.39	14.78	[25]

experimental work,^[25] authors have simulated CsPbI_3 structure with TiO_2 as ETM and Cu_2O as HTM and the thickness of the PVK layer is 450 nm and this device exhibits PCE of 16.23% with relatively less V_{oc} . In this work, $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ is used as a PVK layer and the thickness is 350 nm and the corresponding efficiency is 21.61%. Based on this, it can be concluded that $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ is better PVK matter than CsPbI_3 based on efficiency and the harmful effects on the environment. These parameters can be further enhanced by taking the optimized device thickness (600 nm) and using it at 300 K. For next generation commercialized solar cells, this device can prove to be a worthy candidate. As indicated in Table 6, comprehensive comparative analysis with recently published papers was conducted to gauge similar trends in research.

4. Conclusion

This study uses a device simulator to optimize lead-free PVK solar cells by altering their architecture and material

properties. Various lead-based, tin-based, germanium-based, and tin-germanium-based PVK's were simulated. However, it was found that the FTO/TiO₂/CsSn_{0.5}Ge_{0.5}I₃/Spiro-MeOTAD/Au model exhibits unprecedented superior performance with PCE (21.61%), V_{oc} (1.2 V), J_{sc} (21.32 mA cm⁻²), FF (84.43%) with rectangular shape and width and depth as 0.45 × 0.9 mm². Additionally, a thorough investigation is conducted into the impact of several device factors, such as temperature, thickness, bandgap, and doping concentration, on the simulated device's performance. The optimized values of thickness (600 nm), bandgap (1.45 eV), doping concentration (1 × 10¹⁹ cm⁻³), and temperature (300 K) are found for such PSC. These values are also supported by the corresponding electrical and thermal simulation conducted. The graphs for electric potential and energy bands are also studied and they also support the findings of the article. The design, production, and optimization of significantly more effective environmentally friendly halide-based PSC in the future will be aided by the current computational analysis.

Acknowledgements

D.P. would like to acknowledge MNNIT Allahabad for providing "Institute SEED Grant (Reference no.: 396/R&C/2023-24 dt. 02 September 2023)" for carrying out this research work.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

No data were used for the research described in the article.

Keywords

CsSn_{0.5}Ge_{0.5}I₃, eco-friendly photovoltaics, lead-free, perovskite solar cells, power conversion efficiency, simulation

Received: September 12, 2024

Revised: November 5, 2024

Published online:

- [1] A. Zhang, Y. Chen, J. Yan, *IEEE J. Quantum Electron.* **2016**, 52, 1.
- [2] M. A. Green, A. Ho-Baillie, H. J. Snaith, *Nat. Photonics* **2014**, 8, 506.
- [3] M. A. Peña, J. L. G. Fierro, *Chem. Rev.* **2001**, 101, 1981.
- [4] N. Ashari-Astani, S. Meloni, A. H. Salavati, G. Palermo, M. Grätzel, U. Rothlisberger, *The J. Phys. Chem. C* **2017**, 121, 23886.
- [5] P. Subudhi, D. Punetha, *Prog. Photovoltaics: Res. Appl.* **2023**, 31, 753.
- [6] M. A. Mahmud, T. Duong, J. Peng, Y. Wu, H. Shen, D. Walter, H. T. Nguyen, N. Mozaffari, G. D. Tabi, K. R. Catchpole, K. J. Weber, T. P. White, *Adv. Funct. Mater.* **2022**, 32, 2009164.
- [7] Z. Shi, A. H. Jayatissa, *Materials* **2018**, 11, 729.
- [8] H. S. Jung, N.-G. Park, *Small* **2015**, 11, 10.
- [9] T. Wu, Z. Qin, Y. Wang, Y. Wu, W. Chen, S. Zhang, M. Cai, S. Dai, J. Zhang, J. Liu, Z. Zhou, X. Liu, H. Segawa, H. Tan, Q. Tang, J. Fang, Y. Li, L. Ding, Z. Ning, Y. Qi, Y. Zhang, L. Han, *Nano-Micro Lett.* **2021**, 13, 152.
- [10] H. Dixit, B. Boro, S. Ghosh, M. Paul, A. Kumar, T. Singh, *Phys. Status Solidi A* **2022**, 219, 2100823.
- [11] J. H. Heo, J. Kim, H. Kim, S. H. Moon, S. H. Im, K.-H. Hong, *J. Phys. Chem. Lett.* **2018**, 9, 6024.
- [12] H. Dixit, D. Punetha, S. K. Pandey, *Optik* **2019**, 179, 969.
- [13] W. Zhang, X. Li, S. Fu, X. Zhao, X. Feng, J. Fang, *Joule* **2021**, 5, 2904.
- [14] W. S. Yang, B.-W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, S. S. Shin, J. Seo, E. K. Kim, J. H. Noh, S. I. Seok, *Science* **1979**, 356, 1376.
- [15] P. Subudhi, D. Punetha, *Sci. Rep.* **2023**, 13, 19485.
- [16] K. Fatema, M. S. Arefin, *Opt. Mater.* **2022**, 125, 112036.
- [17] R. Chandel, D. Punetha, D. Dhawan, N. Gupta, *Opt. Quantum Electron.* **2022**, 54, 337.
- [18] S. A. Mhamad, A. M. Mohammed, M. Aziz, F. Aziz, in *Nanostructured Materials for Next-Generation Energy Storage and Conversion*, Springer, **2019**.
- [19] A.-N. Cho, N.-G. Park, *ChemSusChem* **2017**, 10, 3687.
- [20] M. A. Green, Y. Hishikawa, E. D. Dunlop, D. H. Levi, J. Hohl-Ebinger, A. W. Y. Ho-Baillie, *Prog. Photovoltaics: Res. Appl.* **2018**, 26, 427.
- [21] J.-W. Lee, T.-Y. Lee, P. J. Yoo, M. Grätzel, S. Mhaisalkar, N.-G. Park, *J. Mater. Chem. A* **2014**, 2, 9251.
- [22] L. Ji, T. Zhang, Y. Wang, D. Liu, H. Chen, H. Zheng, X. Peng, S. Yuan, Z. D. Chen, S. Li, *Nanoscale* **2022**, 14, 1219.
- [23] N. Sun, W. Gao, H. Dong, Y. Liu, X. Liu, Z. Wu, L. Song, C. Ran, Y. Chen, *ACS Energy Lett.* **2021**, 6, 2863.
- [24] P. Subudhi, V. Sagar, S. Kumar, D. Punetha, *IEEE Sens. J.* **2023**, 23, 28689.
- [25] H. MallaHasan, O. Onay, *Eur. J. Eng. Sci. Technol.* **2022**, 5, 20.
- [26] H. Dixit, D. Punetha, S. K. Pandey, *J. Electron. Mater.* **2019**, 48, 7696.
- [27] F. Behrouznejad, S. Shahbazi, N. Taghavinia, H.-P. Wu, E. Wei-Guang Diao, *J. Mater. Chem. A* **2016**, 4, 13488.
- [28] A. Bag, R. Radhakrishnan, R. Nekovei, R. Jeyakumar, *Sol. Energy* **2020**, 196, 177.
- [29] K. Deepthi Jayan, V. Sebastian, *Sol. Energy* **2021**, 217, 40.
- [30] W. Liao, D. Zhao, Y. Yu, C. R. Grice, C. Wang, A. J. Cimaroli, P. Schulz, W. Meng, K. Zhu, R.-G. Xiong, Y. Yan, *Adv. Mater.* **2016**, 28, 9333.
- [31] N. Singh, A. Agarwal, M. Agarwal, *Superlattices Microstruct.* **2021**, 149, 106750.
- [32] A. Garg, S. Agarwal, D. Punetha, *IEEE Open J. Nanotechnol.* **2024**, 5, 89.
- [33] S. Suman, D. Punetha, S. K. Pandey, *Silicon* **2021**, 13, 1475.
- [34] I. Moeini, M. Ahmadpour, A. Mosavi, N. Alharbi, N. E. Gorji, *Sol. Energy* **2018**, 170, 969.
- [35] S. Zandi, M. Razaghi, *Sol. Energy* **2019**, 179, 298.
- [36] S. Xu, A. Libanori, G. Luo, J. Chen, *iScience* **2021**, 24, 102235.
- [37] H. A. Dewi, J. Li, E. Erdenebileg, H. Wang, M. De Bastiani, S. De Wolf, N. Mathews, S. Mhaisalkar, A. Bruno, *Sustainable Energy Fuels* **2022**, 6, 2428.
- [38] Q. Han, S.-H. Bae, P. Sun, Y.-T. Hsieh, Y. M. Yang, Y. S. Rim, H. Zhao, Q. Chen, W. Shi, G. Li, Y. Yang, *Adv. Mater.* **2016**, 28, 2253.
- [39] Y. Liang, Y. Zang, X. Huang, C. Tian, X. Wang, T. Cui, *J. Phys. Chem. C* **2020**, 124, 8984.
- [40] Y. Zong, N. Wang, L. Zhang, M.-G. Ju, X. C. Zeng, X. W. Sun, Y. Zhou, N. P. Padture, *Angew. Chem., Int. Ed.* **2017**, 56, 12658.
- [41] K. Ahmad, M. A. Gondal, in *Sustainable Materials and Green Processing for Energy Conversion* (Eds: K. Y. Cheong, A. Apblett), Elsevier, **2022**, pp. 341–360.
- [42] S. Li, P. Liu, L. Pan, W. Li, S.-E. Yang, Z. Shi, H. Guo, T. Xia, S. Zhang, Y. Chen, *Sol. Energy Mater. Sol. Cells* **2019**, 199, 75.
- [43] P. Jelimo Chemaoui, P. O. Nyawere, C. M. Maghanga, *Adv. Condens. Matter Phys.* **2023**, 2023, 2902298.
- [44] L.-K. Gao, Y.-L. Tang, X.-F. Diao, *Appl. Sci.* **2020**, 10, 5055.

- [45] S. Sarker, M. T. Islam, A. Rauf, H. Al Jame, M. R. Jani, S. Ahsan, M. S. Islam, S. S. Nishat, K. M. Shorowordi, S. Ahmed, *Sol. Energy* **2021**, 225, 471.
- [46] D. Liu, L. Qiaohong, H. Jing, K. Wu, *J. Phys. Chem. C* **2019**, 123, 3795.
- [47] A. Dubey, K. Mishra, R. Srivastava, A. Kumari, P. K. Jangra, T. K. Joshi, B. L. Choudhary, A. S. Verma, *J. Ovonic Res.* **2024**, 20, 381.
- [48] A. K. Al-Mousoi, M. K. A. Mohammed, S. Q. Salih, R. Pandey, J. Madan, D. Dastan, E. Akman, A. A. Alsewari, Z. M. Yaseen, *Energy Fuels* **2022**, 36, 14403.
- [49] M. S. Adli Azizman, A. W. Azhari, N. Ibrahim, D. S. Che Halin, S. Sepeai, N. A. Ludin, M. N. Md Nor, L. N. Ho, *Heliyon* **2024**, 10, e29676.
- [50] A. Kumar, D. Punetha, S. Chakrabarti, *J. Nanopart. Res.* **2023**, 25, 52.