Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage:
https://semarakilmu.com.my/journals/index.php/fluid_mechanics_thermal_sciences/index
ISSN: 2289-7879

Improvement of Lead-Free Bismuth Based Perovskite Solar Cell Efficiency with Graded Bandgap Structure

Nor Azlian Abdul Manaf[1,*], Wan Yusmawati Wan Yusoff[1], Azuraida Amat[1], Asyraf Hakimi Azmi[2], Mohammad Lamido Madugu[3]

[1] Physics Department, National Defence University of Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia
[2] Faculty of Defence Science and Technology, National Defence University of Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia
[3] Department of Physics, Faculty of Science, Gombe State University, Nigeria

ARTICLE INFO

Article history:
Received 5 September 2024
Received in revised form 22 December 2024
Accepted 3 January 2025
Available online 20 January 2025

Keywords:
Graded bandgap; perovskite solar cells; Bismuth-halide perovskite

ABSTRACT

Lead (Pb) halide perovskite has been identified as a promising light-harvesting material for perovskite solar cells (PSCs) with power conversion efficiency (PCE) exceeding 26%. However, the toxicity of Pb-based materials and poisonous environment are the main hindrances that limit their reliable applications. Bismuth (Bi)-based perovskite has shown high potential to replace conventional Pb-based perovskite, but the PCE of Bi-based perovskite solar cells is far lower than Pb-based. Despite the early exploration of Bi-based materials, a fundamental understanding of the material properties and developing strategies, including device design to improve performance, are needed immediately. Here, we report the graded bandgap design for Bi-halide PSCs, which aims to enhance the output current and PCE by maximizing the solar spectrum through device architecture. Titanium dioxide (TiO_2) was used as an electron transport layer (ETL), and Spiro-OMeTAD was used as a hole transport layer (HTL) due to its facile implementation and high performance in electronic devices. The variation of iodine concentration in bi-doped iodide sets up bandgap tuning and the conductivity type of the layer. This conFigureuration produces cells with desirable performance that effectively absorb the photons in almost all parts of the solar spectrum. Both open circuit voltage (V_{oc}) (940 mV) and fill factors (~58%) for the best cells have shown drastic improvement over single active layer device, and the short current densities (J_{sc}) measured are in the range (20-30) $mAcm^{-2}$. The effects of quasi-electric fields instigated by the graded bandgap structure in the active layers upon the illumination current density and open-circuit voltage of a solar cell will be discussed further.

1. Introduction

Perovskite solar cells (PSCs) are traditionally fabricated in a single bandgap device structure where an active layer, lead-halide, is deposited in between the hole-transport layer (HTL) and electron-transport layer (ETL). This mechanism enables conventional device structures to surpass efficiency of 20%. However, lead (Pb) is recorded by the World Health Organization as a pollutant

---

[*] *Corresponding author.*
E-mail address: azlian@upnm.edu.my

https://doi.org/10.37934/arfmts.126.2.170177

and chemical known to cause birth defects and cancer along with environmental concerns, and its usage is restricted under several international legislations [1,2]. Thus, using Pb-halide PSCs for large-scale development brought controversy within the scientific community.

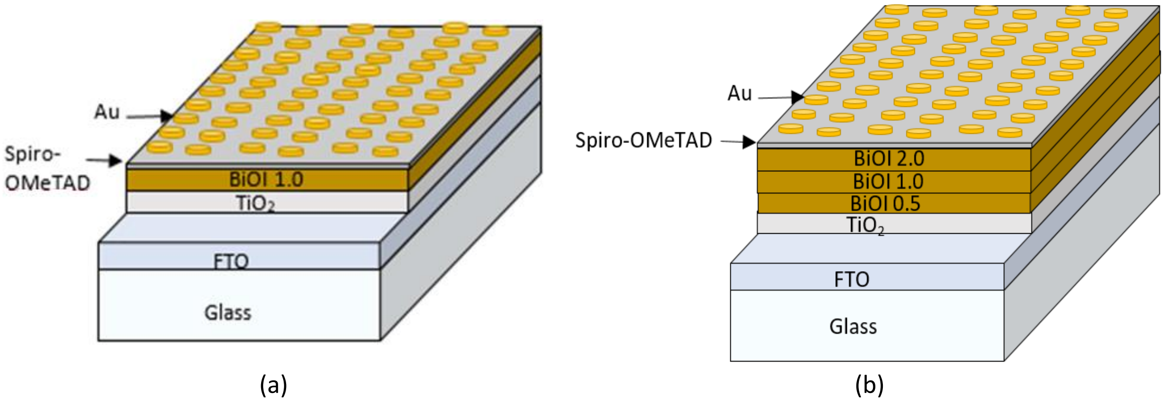
Multiple studies have documented finding*s* on using lead-free materials to replace the Pb in perovskite solar cells without negatively affecting their performance [3]. The essential features of alternative lead-free materials include a direct band gap material with a small exciton binding energy and shallow intrinsic defect levels. Nevertheless, the lead-free PSCs demonstrate low efficiency with less than 4% due to the small output current and instability [2-4]. For example, tin (Sn) halide perovskites can be an alternative material to Pb-halide perovskites. Still, their low current and unsteadiness impede the substitution of Sn-halide for Pb-halide perovskite. The study on indium (In) has been initiated, but the commercial prospects of this alternative have been severely restricted as In-halide perovskites are volatile against reduction-oxidation circumstances [2]. Bismuth halide perovskite has a high-quality state of motion in the electronics field in an electrostatic field and a high tolerance for defect, like conventional Pb-halide. The theoretical Shockley-Queisser Limit (SQL) of bismuth halide perovskite is 22%, showing its potential to compete with conventional PSCs with proper research and development [5,6]. Bismuth halide thin films can be grown using many techniques. Still, among these, modified successive ionic layer adsorption and reaction (SILAR) is more practical since it can produce a highly reliable and repeatable uniform thin film.

Despite early exploration of Bi-halide as an alternative lead-free material for perovskite solar cells, research on graded bandgap perovskite has been approached to enhance the efficacy of light conversion of the solar cell device by changing halide anion concentration and bandgap. Zhu *et al.,* [6] tuning the perovskite absorber layer deposited between gallium nitride (GaN) as an ETL and graphene aerogel as an HTL. This structure produces stable and reproducible solar cells, but the power conversion efficiency (PCE) is still low [6]. Another work on multi-junction tandem cells has been done using a tunable bandgap of methylammonium-lead-halides (MALHs) integrated with crystalline silicon and copper indium gallium selenide (CIGS) [7]. However, it necessitates interconnection between the perovskite sub-cells and complicated electrical coupling, which causes electron-hole recombination centers. Here, we proposed good efficiency of graded bandgap lead-free perovskite solar cells heat treated at optimum temperature based on the prior Bi-halide perovskite thin film characterization. A range of different band gaps is obtained by the compositional engineering of ABX_3 perovskite semiconductors, where methylammonium (MA) is commonly utilized as monovalent A-cations within the perovskite lattice. Increasing iodine concentration in bismuth halide (MA3Bi2I9) would reduce band gaps and change semiconductor behavior from n-type to p-type [8]. In this strategy, the absorbance component consists of three Bi-based perovskite layers with different concentrations of iodine that form n- and p-type homojunctions. This structure enables wide spectrum absorption, leading to a higher J_{sc} value and efficiency beyond the Shockley-Queisser limit (SQL).

2. Methodology

A thin bi-halide perovskite film was deposited using a modified successive ionic layer adsorption and reaction (SILAR) technique. To start synthesizing the solution, two beakers, each containing 50 ml of deionized water, were prepared. The first beaker was added with 0.5 M of bismuth (III) nitrate ($Bi(NO_3)$), while another beaker was added with 0.5 M potassium iodide (KI). Both solutions were stirred for 30 minutes. The third beaker contained deionized water and was prepared as the rinse bath. A glass/ITO substrate was used for this work. It was cleaned thoroughly before the coating process. The coating process started with initially dipping the glass/ITO into the first beaker for 10 s and straight dipping into the second beaker for a chemical reaction for 20 seconds. Finally, the glass/ITO was dipped in the third beaker and rinsed to complete a cycle dipping process. During the dipping process, the substrate was positioned on an inclined beaker. The dipping cycle process was repeated 30 times to obtain a decent layer. The deposited Bi-based perovskite layers were heat treated at various temperatures starting from 250°, 350°, 450° and 550° C. The conductivity of bi-halide perovskite film was studied using four probe Hall effect measurements. In contrast, the microstructural of Bi-halide perovskite thin films has been characterized using a scanning electron microscope (SEM).

The optimum layer was then applied as an active layer in PSCs with the device structure glass/ITO/TiO_2/Bi-halide perovskite/spiro-OMeTAD/Au. Figure 1 shows the schematic of the fabricated Bi-halide perovskite lead-free perovskite solar cells with a single active layer and graded bandgap active layer. An ETL consists of a TiO_2 thin film, and it is deposited on a glass/ITO substrate followed by three layers of Bi-halide perovskite with different concentrations ration of iodine to bismuth. Bi-halide perovskite layer with a half concentration ratio of iodine to bismuth (I:Bi = 0.5:1.0) named Bi-halide 0.5 is deposited as the first perovskite layer. The second perovskite layer comprises the $MA_3Bi_2I_9$ layer with an equal concentration ratio of iodine to bismuth (I: Bi = 1.0: 1.0) named Bi-halide 1.0. Finally, the third perovskite layer is $MA_3Bi_2I_9$ with a double concentration ratio of iodine to bismuth (I: Bi = 2.0: 1.0), named iodine Bi-halide 2.0. The HTL consists of a spiro-OMeTAD, and it was grown using spin coating followed by the top electrode comprising a layer of gold (Au). The conductivity and microstructure of the active layer were studied before the device development. The fabricated device was measured using I-V measurement under a solar spectrum simulator with AM 1.5 illuminations.



(a) (b)

Fig. 1. PSCs device with (a) single absorbance layer and (b) graded bandgap absorbance layer

3. Result

3.1 Thin Film Characterization

Bismuth halide thin films have successfully grown using the SILAR technique and demonstrated good adhesion to the glass substrates. The color of the deposited film changed from yellow to darker orange with an increasing number of dipping cycles, indicating the increase in the film thickness. The quality and homogenous thin films are observed for samples grown at dipping cycles of more than 30 cycles. For this study, a sample grown at 30 cycles was chosen due to the processing time and material used. The films also have been treated with various temperatures from 250°C to 550°C. The as-deposited film was kept as a reference sample. From Figure 2, the color of the film also transformed from dark orange to pale yellow with a higher annealing temperature. The sample annealed at 550°C demonstrated a minor peel-off as a sign that the film cannot have survived in further harsh conditions and higher temperatures than this (≥550°C).

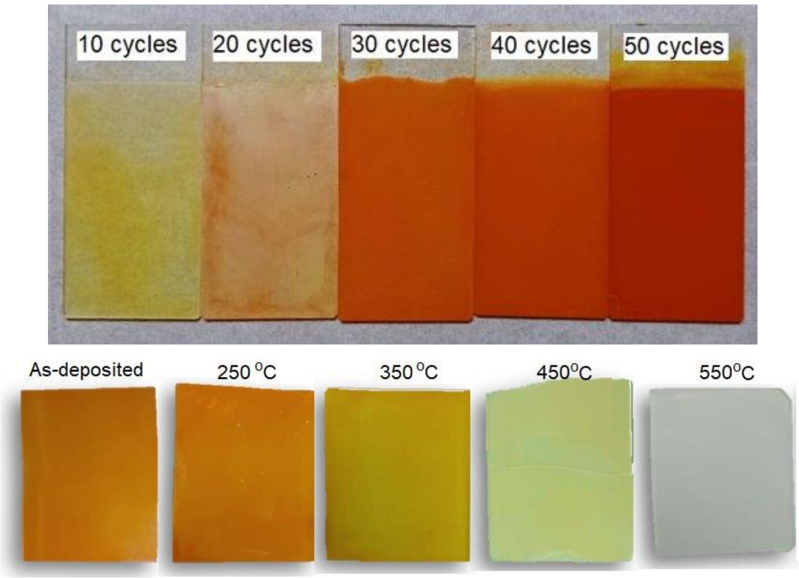


Fig. 2. Physical observation of Bi-halide thin films with various deposition cycles and annealing treatment

Further study on annealing temperature has been done on the electrical conductivity of thin films. The electrical conductivity of the films was calculated from the average resistance obtained from I-V measurement and shown in Figure 3. The SEM images of the as-deposited BiOI layer after heat treatment at 250°C, 350°C, 450°C, and 550°C are also inserted in Figure 3 for better assessment. The graph of conductivity versus heat treatment (Figure 3) shows that the conductivity of as-deposited $MA_3Bi_2I_9$ increased slightly after heat treatment at 250°C. The conductivity increased drastically to its maximum value (1.63×10^4 Sm-1) as the heat treatment temperature increased to 350°C. This trend is related to the enhancement of the size of the flakes shown by the SEM images in microstructural study. SEM image of the as-deposited layer in Figure 3(a) demonstrated small flake agglomerations similar to flower shape. This agglomeration resisted the electron flows due to the grain boundary; thus, the electrical conductivity in as-deposited Bi halide was low. As the heat treatment increased from 250°C to 350°C, the flake size enlarged, as disclosed in Figure 3(b) and Figure 3(c).

From this, we can narrate that the improvement of BiOI conductivity is due to the enlargement of the flakes' size, which reduced the grain boundary and consequently enhanced the electron mobility in BiOI thin films [9,10]. The advantages of having micro-size flakes or columnar in the active layer of solar cell devices have also been reported earlier [11,12].

The BiOI thin film demonstrated the cutback of conductivity value as the samples were heat treated at 450°C and above. This trend is also associated with the microstructure studies presented by SEM images in Figure 3(d) and Figure 3(e). The SEM image of BiOI exposed the shattered flakes microstructure for samples heat treated at 450°C and 550°C. Also, many have reported that the diffusion coefficient of Bi depends on several factors, such as its composition, impurities, annealing temperature, time, and environment [13,14]. With this observation, we believe that heat treatment temperature above 450°C is close to the activation enthalpy point for bismuth out-diffusion.

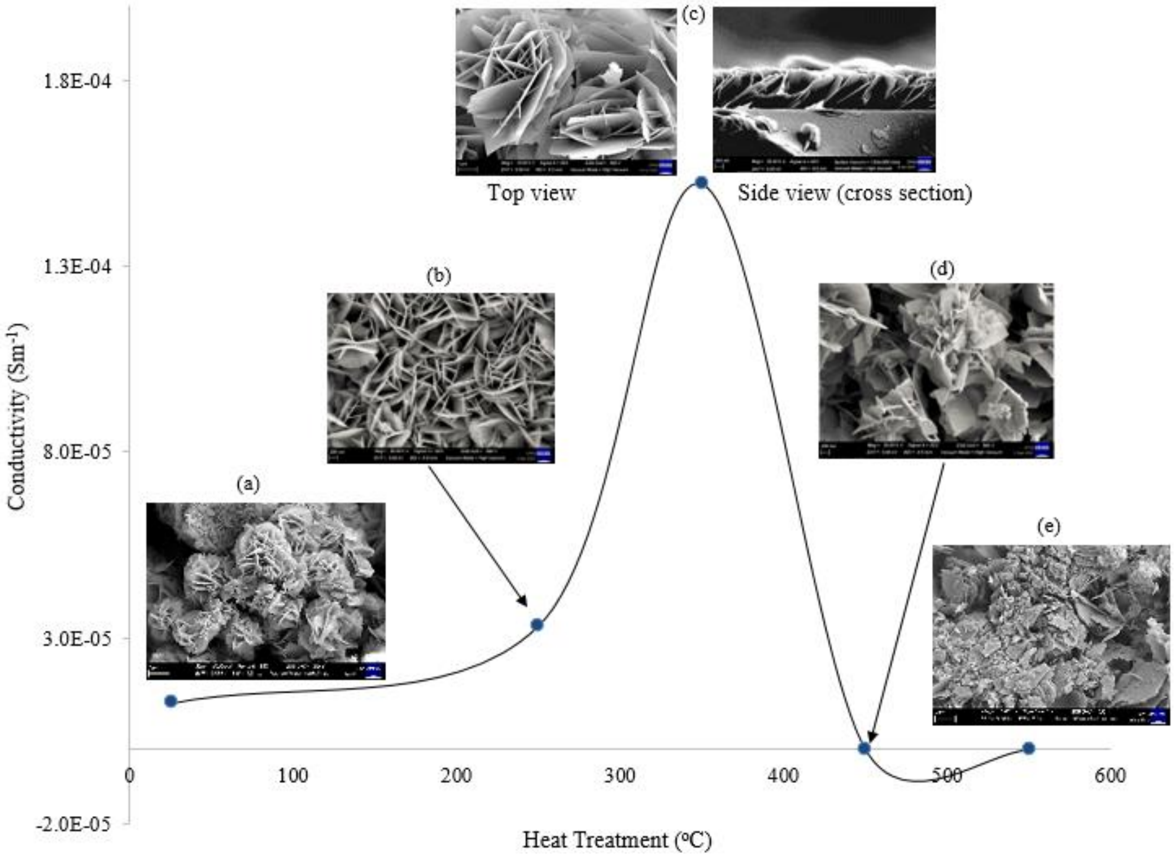


Fig. 3. The graph of electrical conductivity versus heat treatment for bismuth halide perovskite films. The inserted figures are SEM images of the thin films as-deposited and heat-treated at various temperatures

3.2 Solar Cell Measurement

A single active layer solar cell consists of an intrinsic Bi-halide layer with a band gap of 1.66 eV. In the device fabrication, the Bi-halide layer acts as an absorbance layer and is placed in between the n-type of TiO_2 as an electron transport layer (ETL) and the p-type spiro-OMeTAD as a hole transport layer (HTL), as shown in Table 1.

Table 1
PSCs device with single active layer

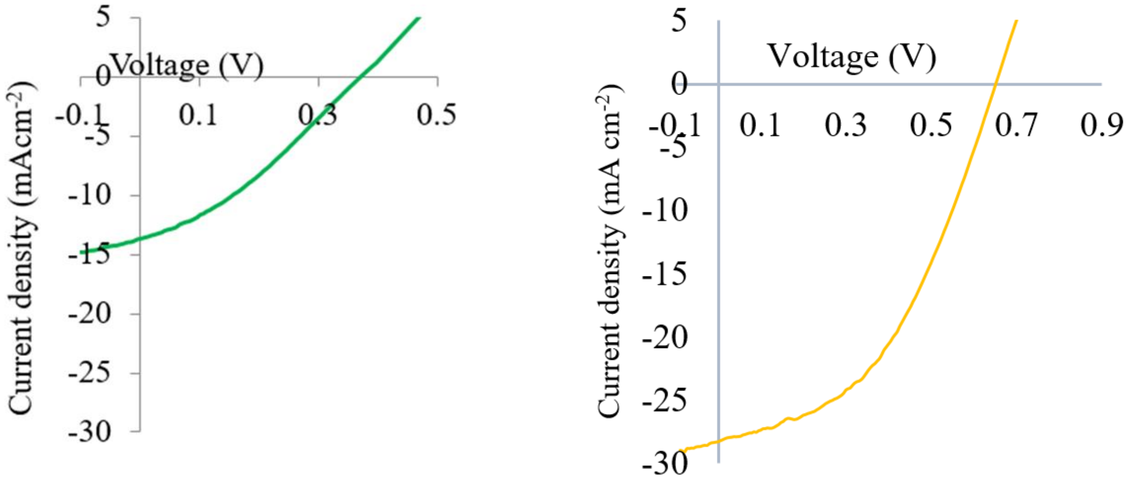
	TiO_2	Bi-halide perovskite layer	Spiro-Ometad
Physical Appearance			
Bandgap Energy	2.83 eV	1.66 eV	1.41 eV
Conductivity Type	n-type	Intrinsic	p-type

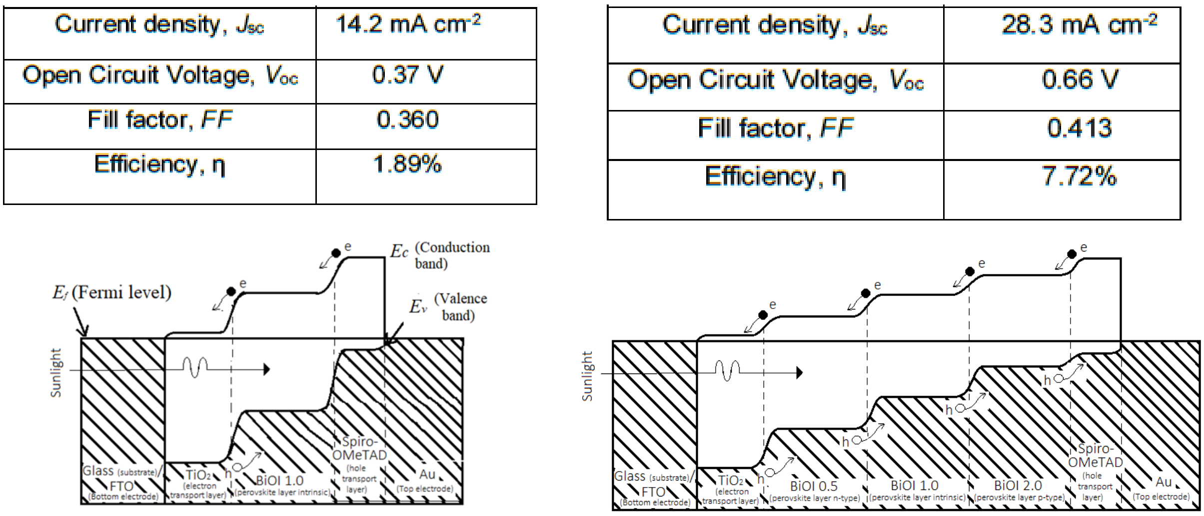
For graded bandgap active layers solar cells, the variation of iodine concentration in bismuth halide establishes the bandgap tuning and conductivity type of the three active layers fabricated between ETL and HTL. The increase of iodine concentration reduces band gaps and induces the change of semiconductor behaviour from n-type to p-type in the active layers, as shown in Table 2 [15].

Table 2
PSCs device with multilayer and graded bandgap active layers

Active layers	TiO_2	BiOI 0.5	BiOI 1.0	BiOI 2.0	Spiro-OMeTAD
Physical Appearance					
Band Energy	2.83 eV	1.80 eV	1.66 eV	1.52 eV	1.41 eV
Conductivity Type	n-type	n-type	Intrinsic BiOL	p-type	p-type

Figure 4 shows that the PSCs with a single active layer (a) were measured with low Jsc, Voc, and efficiency. A solar cell with a single junction can only convert a specific wavelength with the highest efficiency relating to the band gap. In fact, the theoretical limit for power conversion efficiency (PCE) on single-junction solar cells is only about 20% [16]. The PSCs with graded bandgap n-i-p active layers (b) were measured with good current density, J_{sc}, open circuit voltage, $V_{oc,}$ and efficiency, η with ~28.3 $mAcm^{-2}$, ~0.66 V and ~7.72%, respectively. This is due to the device structure with the wider n-type layer placed in front of the device effectively absorbing the photons and more energy from the solar spectrum, leading to an increase in the photoinduced charge separation and electron transfer processes [17,18]. In addition, the bandgap tuning through three perovskite active layers that slowly change from n-type to p-type (variation of iodine concentration in bismuth halide) is so novel since it provides an effective quasi-electric field to speed up drift-diffusion length and enhanced carrier collection [19,20]. The quasi-electric field associated with a graded bandgap active layer in lead-free PSCs structure had better instigated both reduced bulk and surface recombination if the field is in the appropriate direction. In this design, the band gap is reduced towards the back contact device, and the required quasi-electric field should be directed towards the front contact so that electrons drift in the shortest direction [21]. The effects due to the associated quasi-electric field will consequently improve the device's open circuit voltage and current density, simultaneously reducing the recombination at the back contact [19-22].





Current density, J_{sc}	14.2 mA cm^{-2}
Open Circuit Voltage, V_{oc}	0.37 V
Fill factor, *FF*	0.360
Efficiency, η	1.89%

Current density, J_{sc}	28.3 mA cm^{-2}
Open Circuit Voltage, V_{oc}	0.66 V
Fill factor, *FF*	0.413
Efficiency, η	7.72%

(a) (b)

Fig. 4. J-V characteristic of a (a) single active layer solar cell and (b) graded bandgap active layers solar cell

4. Conclusions

The study of the multi-active layer graded bandgap by tuning the bandgap and conductivity type of bismuth halide perovskite as active layers in PSCs has been reported. Theoretically, this configuration could improve performance from the previous (single active layer) design since with this wide bandgap layer at the front, the electromagnetic (EM) spectrum of light (photons) would be effectively absorbed and improve the separation of the charge carriers to the external circuit. This work shows that the device with a graded bandgap structure exhibits high performance (Jsc, Voc, and efficiency) compared to the device with a single layer. Therefore, the findings suggested that the PSC device can be improved through the device architecture of the active layer, where this design has maximized the absorption of solar radiation and minimized the thermalization effect in the solar cell device.

Acknowledgment

This research was funded by a grant from the Ministry of Higher Education of Malaysia (FRGS Grant FRGS/1/2019/STG07/UPNM/02/3) and UPNM/2023/GPPP/SG/7.

References

[1] Correa-Baena, Juan-Pablo, Michael Saliba, Tonio Buonassisi, Michael Grätzel, Antonio Abate, Wolfgang Tress, and Anders Hagfeldt. "Promises and challenges of perovskite solar cells." *Science* 358, no. 6364 (2017): 739-744. https://doi.org/10.1126/science.aam6323

[2] Zhang, Qi, Feng Hao, Jianbao Li, Yangying Zhou, Yaxuan Wei, and Hong Lin. "Perovskite solar cells: must lead be replaced-and can it be done?." *Science and Technology of Advanced Materials* 19, no. 1 (2018): 425-442. https://doi.org/10.1080/14686996.2018.1460176

[3] Jalaludin, Nabilah Ahmad, Khairul Imran Kasirul Kasinathan, Fauziyah Salehuddin, Khairil Ezwan Kaharudin, Faiz Arith, Anis Suhaila Mohd Zain, Ibrahim Ahmad, Siti Aisah Mat Junos, and Prakash R. Apte. "Application of Taguchi-Based GRA Approach for Predictive Modelling of Perovskite Solar Cell." *Journal of Advanced Research in Applied Sciences and Engineering Technology* 59, no. 2 (2024): 99-109. https://doi.org/10.37934/araset.59.2.99109

[4] Low, Pei-Ling, Lavanyah Arumugam, Gregory Soon How Thien, Yew-Keong Sin, Mohd Khairul Ahmad, and Kah-Yoong Chan. "Development of Halide Perovskites for Solar Cell Applications." *Journal of Advanced Research in Applied Sciences and Engineering Technology* 36, no. 1 (2023): 74-82. https://doi.org/10.37934/araset.36.1.7482

[5] Di, Jun, Jiexiang Xia, Huaming Li, Shaojun Guo, and Sheng Dai. "Bismuth oxyhalide layered materials for energy and environmental applications." *Nano Energy* 41 (2017): 172-192. https://doi.org/10.1016/j.nanoen.2017.09.008

[6] Zhu, Huimin, Axel Erbing, Hua Wu, Gabriel J. Man, Soham Mukherjee, Chinnathambi Kamal, Malin B. Johansson, Håkan Rensmo, Michael Odelius, and Erik MJ Johansson. "Tuning the bandgap in silver bismuth iodide materials by partly substituting bismuth with antimony for improved solar cell performance." *ACS Applied Energy Materials* 3, no. 8 (2020): 7372-7382. https://doi.org/10.1021/acsaem.0c00712

[7] Ergen, Onur, S. Matt Gilbert, Thang Pham, Sally J. Turner, Mark Tian Zhi Tan, Marcus A. Worsley, and Alex Zettl. "Graded bandgap perovskite solar cells." *Nature Materials* 16, no. 5 (2017): 522-525. https://doi.org/10.1038/nmat4795

[8] Xiao, Xin, and Wei-De Zhang. "Facile synthesis of nanostructured BiOI microspheres with high visible light-induced photocatalytic activity." *Journal of Materials Chemistry* 20, no. 28 (2010): 5866-5870. https://doi.org/10.1039/c0jm00333f

[9] Kasap, Safa, and Peter Capper, eds. *Springer handbook of electronic and photonic materials*. Springer, 2017. https://doi.org/10.1007/978-3-319-48933-9

[10] Cates, Nichole, and Maria Bernechea. "*Research Update: Bismuth based materials for photovoltaics*." APL Materials 6, no. 8 (2018). https://doi.org/10.1063/1.5026541

[11] Abdul-Manaf, N. A., A. H. Azmi, F. Fauzi, and N. S. Mohamed. "The effects of micro and macro structure on electronic properties of bismuth oxyiodide thin films." Materials Research Express 8, no. 9 (2021): 096401. https://doi.org/10.1088/2053-1591/ac20f7

[12] Kim, Hui-Seon, Anders Hagfeldt, and Nam-Gyu Park. "Morphological and compositional progress in halide perovskite solar cells." *Chemical Communications* 55, no. 9 (2019): 1192-1200. https://doi.org/10.1039/C8CC08653B

[13] Eguchi, Rikuo, Hiroki Yamamuro, and Masayuki Takashiri. "Enhanced thermoelectric properties of electrodeposited Bi_2Te_3 thin films using TiN diffusion barrier layer on a stainless-steel substrate and thermal annealing." *Thin Solid Films* 714 (2020): 138356. https://doi.org/10.1016/j.tsf.2020.138356

[14] Delhaise, André M., and Doug D. Perovic. "Study of solid-state diffusion of Bi in polycrystalline Sn using electron probe microanalysis." *Journal of Electronic Materials* 47 (2018): 2057-2065. https://doi.org/10.1007/s11664-017-6011-x

[15] Matiur, R. M. D., A. A. Abuelwafa, Anissa A. Putri, S. Kato, N. Kishi, and T. Soga. "Annealing effects on structural and photovoltaic properties of the dip-SILAR-prepared bismuth oxyhalides (BiOI, Bi_7O_9I3, Bi_5O_7I) films." SN Applied Sciences 3 (2021): 1-11. https://doi.org/10.1007/s42452-021-04153-y

[16] Alla, Mohamed, Santosh Bimli, Vishesh Manjunath, Manopriya Samtham, Abhishek Kasaudhan, Ekta Choudhary, Mustapha Rouchdi, and Fares Boubker. "Towards lead-free all-inorganic perovskite solar cell with theoretical efficiency approaching 23%." *Materials Technology* 37, no. 14 (2022): 2963-2969. https://doi.org/10.1080/10667857.2022.2091195

[17] Bhandari, Satyapriya, Dibyendu Mondal, S. K. Nataraj, and R. Geetha Balakrishna. "Biomolecule-derived quantum dots for sustainable optoelectronics." *Nanoscale Advances* 1, no. 3 (2019): 913-936. https://doi.org/10.1039/C8NA00332G

[18] Kawano, Yu, Jakapan Chantana, Takahito Nishimura, Abdurashid Mavlonov, and Takashi Minemoto. "Bismuth-doped $Cu(In,Ga)Se_2$ solar cell on flexible stainless steel substrate: Examination of bismuth-doping effectiveness under different substrate temperatures on photovoltaic performances." *Solar Energy* 208 (2020): 20-30. https://doi.org/10.1016/j.solener.2020.07.076

[19] Sun, Haoxuan, Kaimo Deng, Jie Xiong, and Liang Li. "Graded bandgap perovskite with intrinsic n-p homojunction expands photon harvesting range and enables all transport layer-free perovskite solar cells." *Advanced Energy Materials* 10, no. 8 (2020): 1903347. https://doi.org/10.1002/aenm.201903347

[20] Ojo, A. A., W. M. Cranton, and I. M. Dharmadasa. *Next generation multilayer graded bandgap solar cells*. Cham: Springer International Publishing, 2019. https://doi.org/10.1007/978-3-319-96667-0

[21] Dharmadasa, I. M. *Advances in thin-film solar cells*. Jenny Stanford Publishing, 2018. https://doi.org/10.1201/9780429020841

[22] Belhaidouri, Oussama, Rachida Moultif, Laila Mouakkir, Manal Karim, Ahmed Hader, Youssef Lachtioui, and Omar Bajjou. "Optimizing CZTS solar cells efficiency using eco-friendly layers by SCAPS simulation." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 119, no. 2 (2024): 79-90. https://doi.org/10.37934/arfmts.119.2.7990