Applied Physics Letters ARTICLE pubs.aip.org/aip/apl

A method for evaluating spectral down-shifting materials applied to solar cells

Cite as: Appl. Phys. Lett. **123**, 233902 (2023); doi: 10.1063/5.0167959
Submitted: 16 July 2023 · Accepted: 15 November 2023 ·
Published Online: 4 December 2023 · Publisher error corrected: 6 December 2023

Guoxiang Song, Chaogang Lou,[a] Han Diao, and Ruiqi Zhu

AFFILIATIONS

Joint International Research Laboratory of Information Display and Visualization, School of Electronic Science and Engineering, Southeast University, Nanjing 210096, China

[a]Author to whom correspondence should be addressed: lcg@seu.edu.cn

ABSTRACT

Spectral down-shifting materials convert the photons in the solar spectrum that are less efficiently utilized into photons that can be fully used by solar cells, providing an attractive idea for improving the photoelectric conversion efficiency (PCE) of the solar cells. However, there is currently no parameter that can reliably assess the photoelectric excitation effect of the down-shifting materials on solar cells. Here, a calculation method that can reliably evaluate the photoelectric excitation effect of the down-shifting materials on the solar cells is proposed, which introduces the solar spectrum, the quantum yield of materials, and the external quantum efficiency of the solar cells. Then, the calculation method is described in detail with the relevant physical processes, taking the down-shifting materials acting on crystalline silicon solar cells as an example. Finally, the Pearson correlation coefficient between the parametric photoelectric excitation efficiency (PEE) calculated using the method and the ΔPCE value obtained experimentally was 0.999 51, demonstrating the reliability of the calculation method. The PEE calculated using this method is an inherent property of the down-shifting material for a specific solar cell and does not change with external conditions. Therefore, PEE can be used as a parameter for down-shifting materials to facilitate the selection of materials with better effects on solar cells from an enormous number of down-shifting materials and is suitable for various types of solar cells.

With the global energy crisis and environmental pollution becoming increasingly severe, the development of renewable and clean energy is considered to be the way to solve the problem.[1–4] Because solar energy is endless and available everywhere, solar cells are favored for their ability to convert sunlight directly into electricity.[5–8]

However, after the short-wave photons in sunlight are absorbed by the solar cells, a part of their energy becomes heat, which is lost in the form of lattice vibration. In contrast, the long-wave photons cannot be absorbed due to the failure to excite photogenerated carriers. This phenomenon is called spectral mismatch between the solar spectrum and the cell absorption spectra, which is the main reason for limiting the conversion efficiency of solar cells.[9–11] Therefore, how to reasonably modulate the solar spectrum to improve the utilization of solar energy by solar cells, thereby enhancing the PCE of solar cells, has become a vital issue nowadays.

Spectral down-shifting materials can realize the conversion of the photons in the solar spectrum with low utilization efficiency into photons that can be fully used by solar cells so as to improve the PCE of solar cells.[12–14] There already have been many types of down-shifting materials that have been used in solar cells, including rare earth phosphors,[15] quantum dots,[16] and organic dyes.[17] Rare earth phosphors have stable luminescence, quantum dots have high luminescence efficiency, and organic dyes are low-cost and straightforward to prepare. These luminescent materials are widely employed in solar cells for their unique advantages, converting the solar spectrum to increase the efficiency of solar cells. So far, introducing these materials onto the solar cells and observing the improvement of the solar cells is the only way to evaluate the suitability of these materials to the solar cells.[15,18–20] Considering that there are many different types of down-shifting materials and doing experiments needs a longer time, it is necessary to develop a method to evaluate the match between the down-shifting materials and the solar cells.[21,22] Bernal-Correa *et al.* proposed a model for evaluating the performance of solar cells with luminescent down-shifting layers.[23] They considered that the optimal thickness of the down-shifting layers has important effects on the transmittance and reflectance, which vary with the materials and the preparation process, and this makes the evaluation unsuitable.

In this work, we propose a method that evaluates the effects of the down-shifting materials on the solar cells through the solar spectrum, the quantum yield (QY) of the down-shifting materials, and the external quantum efficiency (EQE) of the solar cells. This method makes it easier to select the down-shifting materials suitable for solar

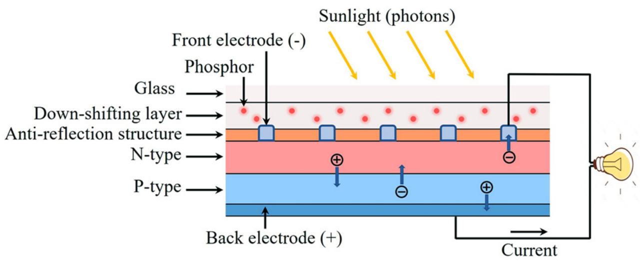

FIG. 1. Schematic diagram of the structure of the solar cell with a down-shifting layer.

cells. In addition, the comparison between the method and experiments is carried out to check the method. The PEE calculated using this method is an inherent property of the down-shifting materials for a specific solar cell and will not depend on the content of the materials, the thickness of the down-shifting layers, packaging process, transmittance and reflectivity. Therefore, PEE can be employed as a parameter for the down-shifting materials, and this parameter can be utilized to easily select the material that can maximize the efficiency of solar cells from a large number of down-shifting materials.

The rare earth down-shifting phosphors YAG:Ce^{3+}, (SrCa)$AlSiN_3$:Eu^{2+}, and $CaAlSiN_3$:Eu^{2+} are used in the experiments. After mixing poly(ethylene-co-vinyl acetate) particles with the phosphors in a mass ratio of 1000:5, the mixture was placed in a crucible and then melted in a muffle furnace at 150 °C, followed by stirring to distribute the phosphors uniformly. Then, the mixture was pressed into a down-shifting film utilizing two polytetrafluoroethylene plates. Finally, the bare solar cells were packaged with the down-shifting films and glass at 150 °C in a vacuum chamber.

The fluorescence spectra of the down-shifting materials were tested with an Ocean Optics Maya 2000Pro. The absorption spectra were performed using a Shimadzu UV-3600i Plus. The *EQE* of the solar cells was tested using a Qtest Station 2000AD (Crowntech). The *QY* was calculated from the luminescence spectra measured in the integrating sphere mode. IEC AAA XJCM-9 of Gsola tester was employed to test the J–V characteristics of the solar cells.

Figure 1 shows the structure of the down-shifting solar cells. The down-shifting layers are located on the upper surface of the solar cells for directly converting short-wave photons into long-wave photons.

The emission spectra of YAG:Ce^{3+}, (SrCa)$AlSiN_3$:Eu^{2+}, and $CaAlSiN_3$:Eu^{2+} are shown in Figs. 2(a)–2(c), respectively. Figures 2(d)–2(f) exhibit their absorption spectra. In Fig. 2(d), the absorption peaks at 346 and 445 nm are attributed to the Ce^{3+}:$^2F_{5/2} \rightarrow 5d_1$, $5d_2$ transition. The broad absorption peaks in Figs. 2(e) and 2(f) are ascribed to Eu^{2+}: $4f^7 \rightarrow 4f^6 5d^1$ transition. Figures 2(g)–2(i) show the cells packaged with each of these three materials as a down-shifting layer (under irradiation with 365 nm UV light).

The whole down-shifting process on the solar cells consists of three main phases. The first is the absorption of the short-wave photons from sunlight by the down-shifting materials. The second is the conversion of the absorbed short-wave photons into the long-wave photons, which are emitted out. The third is that the long-wave photons are absorbed by the solar cells, causing the solar cells to produce a photovoltaic effect. The calculation method was based on these three physical processes. Next, we will discuss the method in detail.

For the first physical process, since the down-shifting layer provides the direct conversion of the sunlight, the solar spectrum should be considered, as shown in Fig. 3(a), where the AM1.5 solar spectrum is used. For the convenience of calculation, the solar spectrum is converted into relative photon counts, as shown in Fig. 3(b). The relative photon counts of the AM1.5 solar spectrum are denoted by *SS*.

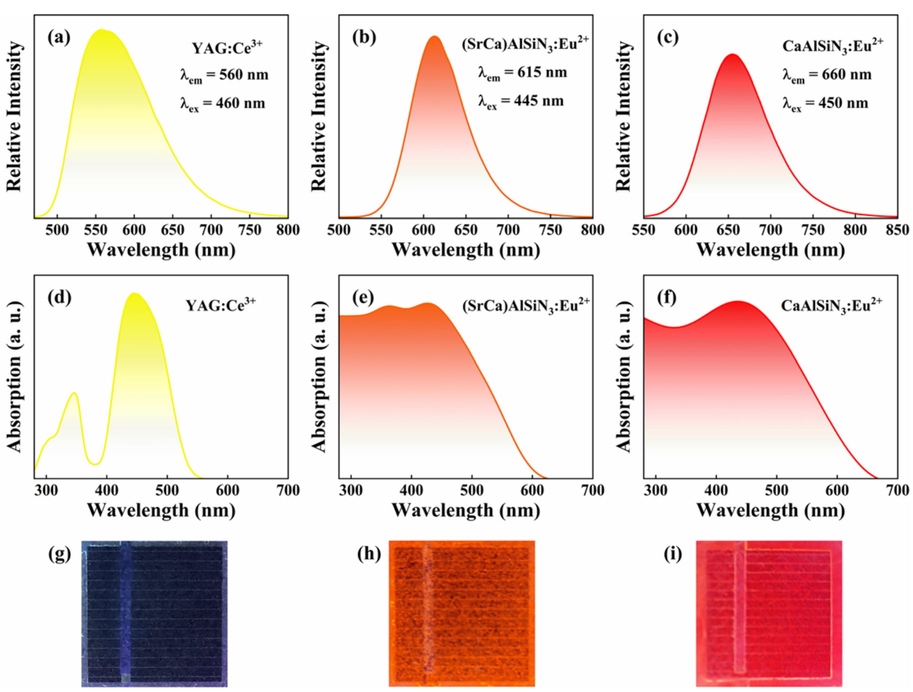

FIG. 2. The emission spectra of (a) YAG:Ce^{3+}, (b) (SrCa)$AlSiN_3$:Eu^{2+}, and (c) $CaAlSiN_3$:Eu^{2+}. The absorption spectra of (d) YAG:Ce^{3+}, (e) (SrCa)$AlSiN_3$:Eu^{2+}, and (f) $CaAlSiN_3$:Eu^{2+}. The packaged solar cell with (g) YAG:Ce^{3+}, (h) (SrCa)$AlSiN_3$:Eu^{2+}, and (i) $CaAlSiN_3$:Eu^{2+} as the down-shifting layer, respectively.

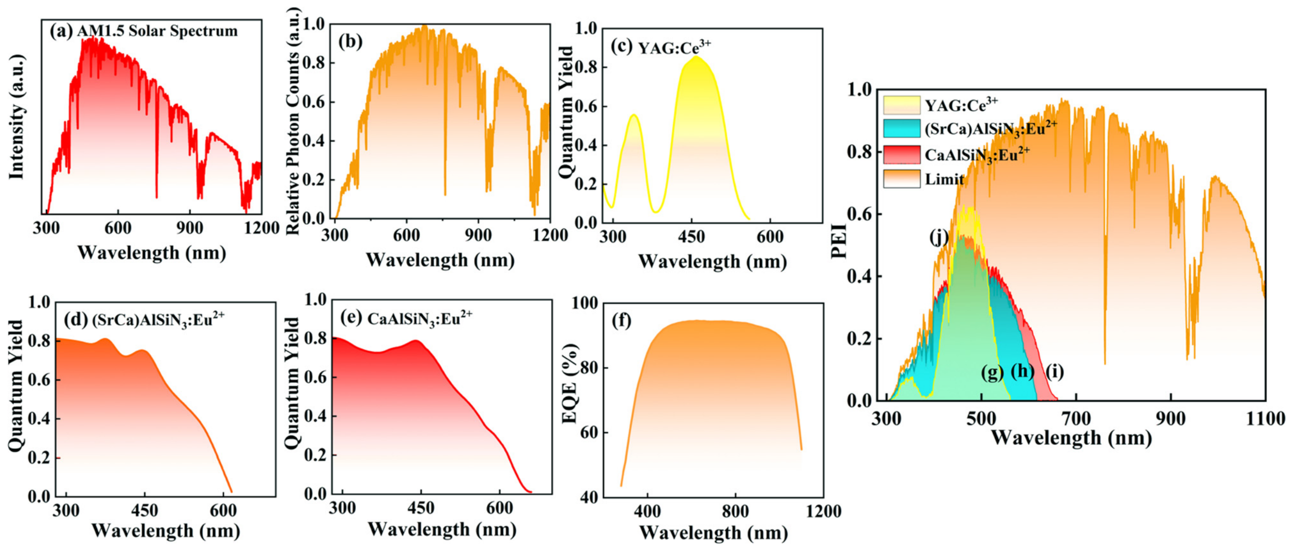

FIG. 3. (a) AM1.5 solar spectrum. (b) Relative photon counts of the AM1.5 solar spectrum. The quantum yield of (c) YAG:Ce^{3+}, (d) (SrCa)$AlSiN_3$:Eu^{2+}, and (e) $CaAlSiN_3$:Eu^{2+}. (f) External quantum efficiency of silicon solar cells. The *PEI* of (g) YAG:Ce^{3+}, (h) (SrCa)$AlSiN_3$:Eu^{2+}, and (i) $CaAlSiN_3$:Eu^{2+}. (j) The maximum limit of *PEI*.

For the second physical process, there is energy loss in the conversion of the short-wave photons into the long-wave photons, so *QY* needs to be introduced here. The *QY* of the luminescent material is defined as the ratio of the number of the emitted photons to the number of the incident photons, which can be expressed by the following equation:[24]

$$QY = \frac{N_{out}}{N_{in}}, \tag{1}$$

where N_{out} is the number of the photons emitted by the down-shifting material, and N_{in} is the number of the incident photons. The *QY* of YAG:Ce^{3+}, (SrCa)$AlSiN_3$:Eu^{2+}, and $CaAlSiN_3$:Eu^{2+} is shown in Figs. 3(c)–3(e).

For the third physical process, the long-wave photons are used to excite carriers in the solar cells, so the *EQE* of the solar cells is also important. The *EQE* is defined as the ratio of the number of the excited carriers to the number of the photons hitting the solar cells and can be expressed by the following equation:[25]

$$EQE = \frac{M_{out}}{M_{in}}, \tag{2}$$

where M_{out} is the number of the excited carriers, and M_{in} is the number of the incident photons. In this work, the *EQE* of silicon solar cells shown in Fig. 3(f) is used for the calculation.

After the above-mentioned analysis, the photoelectric excitation intensity (*PEI*) of the down-shifting materials on the solar cells can be expressed by the following equation:

$$PEI = SS \times QY \times EQE. \tag{3}$$

PEI is the relative number of photogenerated carriers produced by the solar cells after the sunlight passes through the spectral conversion effect of the down-shifting materials. The *PEI* of YAG:Ce^{3+}, (SrCa)$AlSiN_3$:Eu^{2+}, and $CaAlSiN_3$:Eu^{2+} is shown in Figs. 3(g)–3(i), respectively. Assuming that there exists an ideal down-shifting material with the *QY* of 1 at any wavelength, the *PEI* of this ideal material is shown in Fig. 3(j), and the PEI at this point represents the maximum limit of *PEI*.

Integrating the *PEI* of the down-shifting materials and the ideal material separately, we can establish the following equation:

$$PEE = \frac{\int SS \times QY \times EQE}{\int SS \times QY_L \times EQE}, \tag{4}$$

where QY_L is the ideal quantum yield, which is 1. PEE is the ratio of PEI to the ideal PEI, which represents the photoelectric excitation efficiency of the down-shifting materials to the solar cell. The PEE value directly reflects the photoelectric excitation effect of the down-shifting material on the solar cell. The method was used to calculate the *PEE* of the solar cells packaged with YAG:Ce^{3+}, (SrCa)$AlSiN_3$:Eu^{2+}, and $CaAlSiN_3$:Eu^{2+}, respectively, as 11.673%, 16.199%, and 18.431%.

To verify the reliability of this calculation method, the J–V characteristics of the cells packaged with YAG:Ce^{3+}, (SrCa)$AlSiN_3$:Eu^{2+}, and $CaAlSiN_3$:Eu^{2+} were tested and compared with the bare cells, as shown in Figs. 4(a)–4(c). Table I shows the detailed electrical parameters. J_{sc} is the short circuit current density, V_{oc} is the open circuit voltage, *FF* is the fill factor, P_{max} is the maximum power, *PCE* is the photovoltaic conversion efficiency, and ΔPCE is the relative growth of the photovoltaic conversion efficiency.

Detailed data on *PEE* and ΔPCE are shown in Fig. 4(d). As seen from the purple curve, $CaAlSiN_3$:Eu^{2+} has the largest *PEE* value, indicating that $CaAlSiN_3$:Eu^{2+} has the best photoelectric excitation effect on the silicon solar cells compared to YAG:Ce^{3+} and (SrCa)$AlSiN_3$:Eu^{2+}. On the contrary, YAG:Ce^{3+} has the worst photoelectric excitation effect on solar cells. From the blue curve, it can be seen that $CaAlSiN_3$:Eu^{2+} has the largest ΔPCE value, while YAG:Ce^{3+} has the

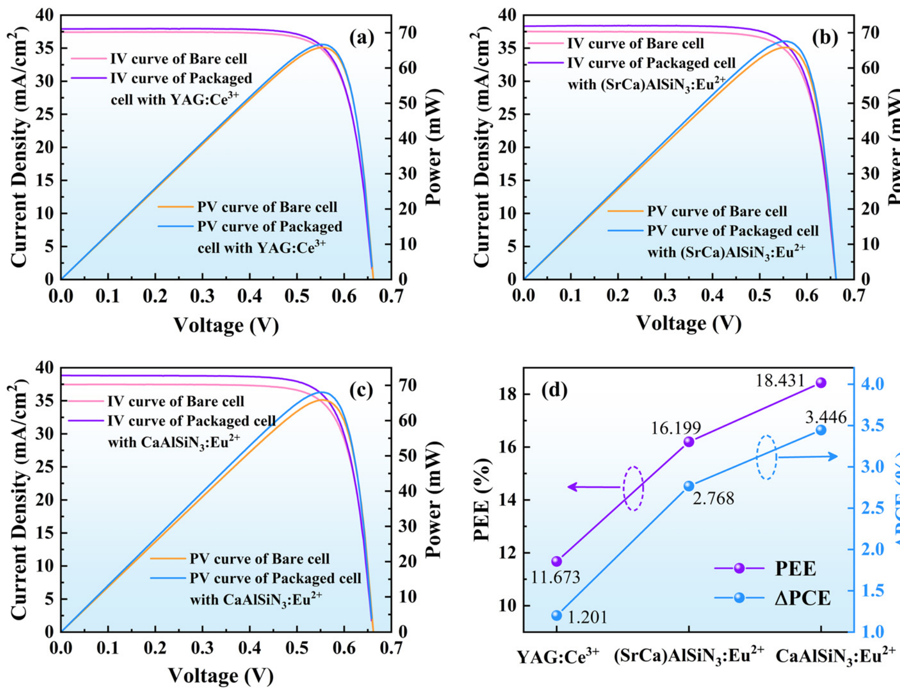

FIG. 4. J–V characteristics of the solar cells packaged with (a) YAG:Ce^{3+}, (b) (SrCa)$AlSiN_3$:Eu^{2+}, and (c) $CaAlSiN_3$:Eu^{2+}. (d) Detailed data on *PEE* and Δ*PCE* of solar cells packaged with YAG:Ce^{3+}, (SrCa)$AlSiN_3$:Eu^{2+}, and $CaAlSiN_3$:Eu^{2+}.

smallest Δ*PCE*. In addition, it can be seen that the curves of *PEE* and Δ*PCE* have the same trend of variation. Here, in order to compare the two sets of data more directly, we calculated the correlation between the two sets of data using the Pearson correlation coefficient, which was 0.999 51. This proves that the PEE values calculated by the method proposed in this Letter have a strong correlation with the ΔPCE values obtained by the experiment and verify the reliability of the method. The above-mentioned results indicate that PEE can accurately reflect the photoelectric excitation effect of the down-shifting materials on solar cells. In addition, it can be seen from Eq. (4) that the physical parameters used to calculate the PEE are all definite values and will not change with external conditions. Therefore, the calculated PEE value is an inherent property of the down-shifting materials for a specific solar cell.

Finally, we tested the EQE of the bare and packaged cells, as shown in Fig. 5(a). Obviously, compared to the bare cells, the EQE of the packaged cells has a significant increase in the short-wavelength part, which is ascribed to the role of the down-shifting materials that absorb the short-wavelength photons and release the long-wavelength photons. In addition, it can be seen that $CaAlSiN_3$:Eu^{2+} has the best effect compared to the other two materials. Figure 5(b) shows a partial enlargement of Fig. 5(a) in the long-wavelength part. It can be seen that the EQE of the packaged cell decreases slightly in the long-wavelength part because the scattering of the down-shifting particles reduces the transmittance. The integrated J_{sc} of the bare and packaged cells was calculated from the EQE, as shown in Figs. 5(c)–5(f). The integrated J_{sc} of the bare cell and the cells packaged with YAG:Ce^{3+}, (SrCa)$AlSiN_3$:Eu^{2+}, and $CaAlSiN_3$:Eu^{2+} is 39.08, 39.28, 39.47, and 39.71 mA/cm^2, respectively.

This work presents a calculation method that can evaluate the photoelectric excitation efficiency of the down-shifting materials on the solar cells. The parametric PEE values obtained by using this method can conveniently and accurately select the materials that can improve the efficiency of the solar cells from a variety of luminescent materials, and the method is applicable to all types of solar cells. The calculation method utilizes the actual physical process of the down-shifting materials acting on the solar cells, introducing physical

TABLE I. The detailed electrical parameters of bare and packaged solar cells. Ten samples of each type of battery were prepared, and the test results were averaged.

Materials for packaging		J_{sc} (mA/cm^2) ±0.01	V_{oc} (V) ±0.001	*FF* (%) ±0.1	P_{max} (mW) ±0.01	*PCE* (%) ±0.01	Δ*PCE* (%)
YAG:Ce^{3+}	Bare cell	37.50	0.661	77.2	65.50	19.15	1.201
	Packaged	37.84	0.661	77.4	66.26	19.38	
(SrCa)$AlSiN_3$:Eu^{2+}	Bare cell	37.50	0.661	77.2	65.50	19.15	2.768
	Packaged	38.49	0.661	77.5	67.32	19.68	
$CaAlSiN_3$:Eu^{2+}	Bare cell	37.50	0.661	77.2	65.50	19.15	3.446
	Packaged	38.61	0.661	77.6	67.75	19.81	

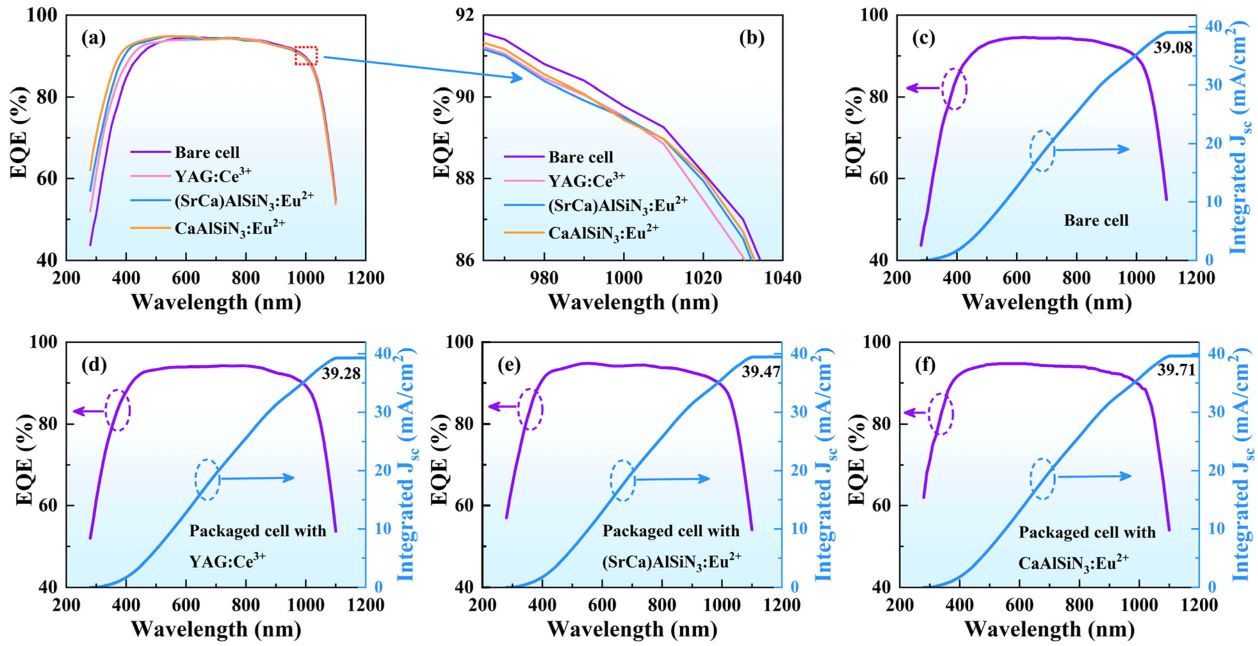

FIG. 5. (a) EQE of bare cell and EQE of the packaged solar cell with YAG:Ce^{3+}, (SrCa)$AlSiN_3$:Eu^{2+}, and $CaAlSiN_3$:Eu^{2+} as the down-shifting layer, respectively. (b) Partial enlargement of (a). (c) EQE and integrated J_{sc} of bare cell. EQE and integrated J_{sc} of the packaged solar cell with (d) YAG:Ce^{3+}, (e) (SrCa)$AlSiN_3$:Eu^{2+}, and (f) $CaAlSiN_3$:Eu^{2+} as the down-shifting layer, respectively.

quantities such as solar spectrum, QY, and EQE. Moreover, the calculated PEE values show the same pattern as the experimentally obtained ΔPCE values with a strong correlation, which verifies the reliability of the calculation method. Finally, the test results of EQE and integrated J_{sc} intuitively reflect the enhancement effect of the down-shifting materials on the solar cells in the short-wave part.

This study was supported by the Primary Research & Development Plan of Jiangsu Province (Grant No. BE2016175).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Guoxiang Song: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Chaogang Lou:** Conceptualization (equal); Funding acquisition (equal); Methodology (equal); Writing – review & editing (equal). **Han Diao:** Data curation (equal); Formal analysis (equal). **Ruiqi Zhu:** Data curation (equal); Investigation (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] H. Lin, M. Yang, X. Ru, G. Wang, S. Yin, F. Peng, C. Hong, M. Qu, J. Lu, L. Fang, C. Han, P. Procel, O. Isabella, P. Gao, Z. Li, and X. Xu, Nat. Energy **8**, 789 (2023).
[2] X. Chen, Q. Luo, and C. Ma, Chin. J. Polym. Sci. **41**, 1169 (2023).
[3] W. Wang, X. Liu, J. Wang, C. Chen, J. Yu, D. Zhao, and W. Tang, Adv. Energy Mater. **13**, 2300694 (2023).
[4] H. K. G. Singh, K. Matsumoto, and A. Sakurai, Appl. Phys. Lett. **121**, 173906 (2022).
[5] K. Aitola, G. G. Sonai, M. Markkanen, J. J. Kaschuk, X. Hou, K. Miettunen, and P. D. Lund, Sol. Energy **237**, 264 (2022).
[6] M. Nakamura, C. C. Lin, C. Nishiyama, K. Tada, T. Bessho, and H. Segawa, ACS Appl. Energy Mater. **5**, 8103 (2022).
[7] Q. Li, C. Monticelli, and A. Zanelli, Renew. Energy **195**, 906 (2022).
[8] B. P. Veettil, Y. Zhang, D. Payne, M. Juhl, S. Huang, B. Hallam, and D. Bagnall, Appl. Phys. Lett. **122**, 142101 (2023).
[9] M. A. Cardoso, S. Correia, A. R. Frias, H. Goncalves, R. Pereira, S. C. Nunes, M. Armand, P. S. Andre, V. D. Bermudez, and R. Ferreira, J. Rare Earths **38**, 531 (2020).
[10] Y. Yu, L. Lan, and H. Cai, J. Phys. Chem. C **122**, 96 (2018).
[11] Y. Tai, B. Pan, X. Li, Z. Nie, X. Du, and G. Yuan, RSC Adv. **8**, 37396 (2018).
[12] Z. Feng, S. Jiang, X. Luo, J. Shen, Y. Pang, L. Li, and X. Zhou, Opt. Mater. **62**, 348 (2016).
[13] W. Ho, J. Liu, and B. Ke, Materials **15**, 452 (2022).
[14] M. H. Soltani, A. Reyhani, A. Taherkhani, S. Mirershadi, and S. Z. Mortazavi, J. Mater. Sci. **32**, 15675 (2021).
[15] H. Diao, C. Lou, Z. Wang, S. Razzaq, A. Asghar, S. Huang, Y. Yin, Y. Tian, L. Li, and X. Sun, J. Lumin. **260**, 119830 (2023).
[16] R. Lopez-Delgado, H. J. Higuera-Valenzuela, A. Zazueta-Raynaud, A. Ramos-Carrazco, J. E. Pelayo, D. Berman-Mendoza, M. E. Alvarez-Ramos, and A. Ayon, Microsyst. Technol. **24**, 495 (2018).

[17]A. P. Perdomo, R. V. Fernandes, N. J. A. Cordeiro, F. Franchello, M. A. T. da Silva, J. L. Duarte, and E. Laureto, J. Appl. Phys. **128**, 035502 (2020).
[18]Y. Kim, H. Jeong, S. Kim, Y. H. Song, B. Y. Kim, J. P. Kim, B. K. Kang, J. Yun, and J. Jang, Nanoscale **12**, 558 (2020).
[19]W. Ho, G. Li, J. Liu, Z. Lin, B. You, and C. Ho, Appl. Surf. Sci. **436**, 927 (2018).
[20]E. D. Jung, C. U. Kim, Y. W. Noh, S. K. Seo, Y. I. Noh, K. J. Choi, and M. H. Song, EcoMat **5**, e12399 (2023).
[21]J. Y. Huang, Y. Wang, G. T. Fei, S. H. Xu, B. Wang, and Z. Zeng, Colloid Surf., A **652**, 129907 (2022).
[22]L. Meng, L. Shi, Y. Ge, J. Tang, Y. Chen, and H. Zhong, Sol. Energy Mater. Sol. Cells **220**, 110856 (2021).
[23]R. Bernal-Correa, A. Morales-Acevedo, and J. Montes-Monsalve, Phys. Scr. **98**, 065904 (2023).
[24]M. J. Deutsch and H. Park, Synth. Met. **269**, 116548 (2020).
[25]W. Ho, Y. Lee, and S. Su, Nanoscale Res. Lett. **9**, 483 (2014).