Perovskite/CIGS Spectral Splitting Double Junction Solar Cell with 28% Power Conversion Efficiency

HIGHLIGHTS
CIGS bottom solar cells with $E_g$ ranging from 1.02 to 1.14 eV are prepared
The lower the $E_g$ of CIGS bottom cell, the higher PCE of PVK/CIGS tandem solar cell
PCE of 28% was demonstrated in a 1 cm$^2$-sized PVK/CIGS 4-Terminal solar cell
The result can be utilized to design better tandem solar cell in the future
Perovskite/CIGS Spectral Splitting Double Junction Solar Cell with 28% Power Conversion Efficiency

Motoshi Nakamura,1,2 Keishi Tada,3 Takumi Kinoshita,3 Takeru Bessho,2 Chie Nishiyama,2 Issei Takenaka,1 Yoshinori Kimoto,1 Yuta Higashino,1 Hiroki Sugimoto,1 and Hiroshi Segawa2,3,4,*

SUMMARY
The highest theoretical efficiency of double junction solar cells is predicted for architectures with the bottom cell bandgap (E_g) of approximately 0.9–1.0 eV, which is lower than that of a typical Si cell (1.1 eV). Cu(In,Ga)(Se,S)2 (CIGS) solar cells exhibit a tunable E_g depending on their elemental composition and depth profile. In this study, various CIGS solar cells with E_g ranging from 1.02 to 1.14 eV are prepared and a spectrum splitting system is used to experimentally demonstrate the effect of using lower-E_g cells as the bottom cell of two-junction solar cells. The four-terminal tandem cell configuration fabricated using a mixed-halide perovskite top cell (E_g = 1.59 eV; stand-alone efficiency = 21.0%) and CIGS bottom cell (E_g = 1.02 eV; stand-alone efficiency = 21.5%) with a 775-nm spectral splitting mirror exhibits an efficiency of 28.0% at the aperture area of 1 cm^2.

INTRODUCTION
Improving the power conversion efficiency (PCE) of solar cells is essential for reducing the solar power cost (Peters et al., 2019). Solar cells with single-junction structures have reached the theoretical limit of PCE, and the possibility of further improvement of PCE is significantly low (Shockley and Queisser, 1961; Green et al., 2020). One of the approaches for overcoming this limitation is the introduction of tandem structures, where two or more solar cells with different bandgaps (E_g) are stacked while optimizing the wavelength absorption range. In this method, depending on the number of cells used, the theoretical PCE limit can be exceeded up to 50% (Meillaud et al., 2006; Alharbi and Kais, 2015). In fact, a PCE of approximately 40% was reported for III-V multi-junction cells (Green et al., 2020). However, the III-V semiconductor-based tandem devices are expensive, which limits their current applications to only a few markets, such as the space industry (Bosi and Pelosi, 2007).

For attaining a high PCE without an excessive cost, double junction devices that are constructed with perovskite (PVK) solar cells as top cells and Si (Chen et al., 2020; Uzu et al., 2015; Duong et al., 2020; Xu et al., 2020; Jaysankar et al., 2019b; Wang et al., 2020), Cu(In,Ga)(Se,S)2 (CIGS) (Kim et al., 2019; Gharibzadeh et al., 2020; Shen et al., 2018; Jiang et al., 2020; Jaysankar et al., 2019a; Al-Ashouri et al., 2019; Han et al., 2018), PVK (Tong et al., 2019; Lin et al., 2019; Palmstrom et al., 2019; Zhao et al., 2018; Yao et al., 2020; Abdullahi Nejand et al., 2020; Yang et al., 2019), and dye-sensitized (DS) (Kinoshita et al., 2015; Hosseinnezhad 2019) solar cells as bottom cells have garnered considerable attention recently. Although a higher PCE has been reported for the PVK/Si combination, the optimal E_g of the bottom cell in the double junction devices ranges from 0.9 to 1.0 eV (see Figure S1), which is lower than the typical E_g of crystalline Si solar cells (1.1 eV). However, depending on their elemental compositions and depth profiles, CIGS solar cells possess a tunable E_g which can be as low as 1.0 eV (Nakamura et al., 2019), close to the optimal value of the bottom cell for both two-terminal (2-T) and four-terminal (4-T) tandem solar cells. In this study, we experimentally show that the PCE of the double junction solar cells is higher when the bottom cell E_g is closer to 1.0 eV, as predicted by theoretical studies. Subsequently, we conclude that CIGS solar cells are potentially the most superior among the choices as the bottom cell of Perovskite-based double junction solar cells.

RESULTS AND DISCUSSION
The tandem solar cell with a spectral splitting system was constructed using a PVK top cell, CIGS bottom cell, and a dichroic mirror that was fixed at an angle of 45°, as schematically shown in Figure 1.
The layered structure of the fabricated 0.995 cm²-aperture sized PVK cell was Fluorine-doped tin oxide (FTO)/c-TiO₂/m-TiO₂/PVK/Spiro-OMeTAD/Au, where the composition of PVK was selected as \([K_{0.05}(FA_{0.85}MA_{0.15})_{0.95}]\text{Pb}(I_{0.85}Br_{0.15})_3\). The fabrication using mixed halide and alkali metal-doped mixed cation PVK has several advantages, the details of which are described elsewhere (Tang et al., 2017; Lu et al., 2020). However, the main reasons of using the PVK include an increase in the efficiency and reduction of the hysteresis in the current density-voltage (J-V) characteristics. The external quantum efficiency (EQE) spectrum and J-V curve of the fabricated PVK cell measured under the standard 1-sun condition (i.e., without using the dichroic mirror) are shown in Figures 2A and 2B, respectively. The \(E_g\) of the PVK cell was determined to be 1.59 eV using the peak position of the first order derivative of the EQE curve \((-d(\text{EQE})/d\lambda)\) (Kruckemeier et al., 2020), which is an ideal value for the top cell of a two-junction tandem solar cell (see Figure S1). The efficiency of the fabricated 1 cm²-aperture sized PVK cell measured under 1,000 W/m² in the reverse J-V scan was 21.0% with \(J_{sc}\), \(V_{oc}\), and FF of 22.7 mA cm⁻², 1,181.8 mV, and 78.1%, respectively. The efficiency of the cell in the forward J-V scan was measured to be 20.3% with \(J_{sc}\), \(V_{oc}\), and FF of 22.6 mA cm⁻², 1,173.8 mV, and 76.5%, respectively.

CIGS bottom cells with an aperture area of 1.04 cm² were fabricated using the sulfurization after selenization (SAS) process, where a Copper-Gallium/Indium metal precursor on a glass/Molybdenum substrate was selenized with \(H_2Se\) gas followed by sulfurization with \(H_2S\) gas in a closed furnace. More than 100 CIGS cells with various \(E_g\) values were prepared by adjusting the elemental depth profile of the CIGS absorber layer via tuning some of the parameters in the SAS process, as described in a previous study (Nakamura et al., 2019). Among these cells, four CIGS cells with approximately the same efficiencies (21.5 ± 0.3%) and FFs (75 ± 2%) but with different \(E_g\) values ranging from 1.02 to 1.14 eV were used for constructing the tandem structure. The normalized EQE spectra and J-V curves of these four CIGS cells are shown in Figures 2C and 2D, respectively. Unlike PVK cells, CIGS cells generally showed negligible hysteresis; therefore, we displayed the J-V curves in the forward direction only. The device parameters are summarized in Table 1. The elemental depth profiles measured by glow discharge optical emission spectroscopy and calculated \(E_g\) depth profiles using an empirical equation are shown in Figure S2 (Bär et al., 2004).

The J-V curves and EQE spectra of the PVK top cell and the CIGS bottom cells measured using the dichroic mirror with splitting wavelength of 775 nm are shown in Figure 3, and the device parameters are summarized in Table 2. The splitting edge wavelength of the dichroic mirror was selected because 775 nm (or 1.60 eV) approximately matches the \(E_g\) of the PVK top cell (1.59 eV). The PCE of the PVK cell reduced from 21.0% to 19.1% because of the reduced \(J_{sc}\) and FF when the mirror was used. This reduction is reasonable considering that there are parasitic optical losses in the mirror as well as the slight mismatch between the splitting wavelengths and the \(E_g\) of the PVK cell. Nevertheless, retaining greater than 90% of the original PCE implies that the spectrum splitting system is well designed with the appropriate choice of wavelength. The PCE of all CIGS bottom cells with different \(E_g\) were almost the same when measured without
the mirror, as shown in Table 1. Moreover, cells with a lower $E_g$ showed a higher efficiency when measured with the mirror. Finally, the PCE difference of the cells with $E_g$ of 1.02 and 1.14 eV reaches as high as 1.4%. This experimental value is in good agreement with the theoretical results, obtained from the detailed balanced calculations shown in Figure 4 (De Vos, 1980). The same trend was observed when the CIGS bottom cells were measured under dichroic mirrors with other splitting wavelengths (see Figure S3). To the best of our knowledge, this is the first report on the experimental procedure and evaluation of the advantage of using low-$E_g$ CIGS as the bottom cell of a tandem device with PVK solar cells.

The overall PCE of the 4-T tandem cell with the spectral splitting system is 28%, comprising the PVK top cell with 19.1% PCE and the lowest-$E_g$ CIGS bottom cell with 8.9% PCE. This is one of the highest reported PCE for the experimentally fabricated PVK-based tandem solar cells (see Table S1).

CONCLUSION
In this study, we experimentally demonstrated that the PCE of a double junction solar cell is higher when the $E_g$ of the bottom cell is closer to 1.0 eV, as predicted theoretically. The device PCE was proven to be increased by an absolute 1.4% when the bottom cell $E_g$ reduced from 1.14 to 1.02 eV. This result indicated

|        | PCE (%) | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (mV) | FF (%) |
|--------|---------|------------------------|--------------|--------|
| PVK-Rvs. | 21.0    | 22.7                   | 1,181.8      | 78.1   |
| PVK-Frd. | 20.3    | 22.6                   | 1,173.8      | 76.5   |
| CIGS ($E_g$ = 1.14 eV) | 21.6    | 39.1                   | 728.8        | 75.7   |
| CIGS ($E_g$ = 1.11 eV) | 21.8    | 39.8                   | 715.1        | 76.5   |
| CIGS ($E_g$ = 1.08 eV) | 21.5    | 41.0                   | 708.9        | 74.1   |
| CIGS ($E_g$ = 1.02 eV) | 21.5    | 43.6                   | 659.0        | 74.8   |

Table 1. Parameters of the PVK and CIGS Solar Cells Extracted from the J-V Curves and EQE Spectra in Figure 2
the potential superiority of PVK/CIGS tandem solar cells over PVK/Si cells because a crystalline Si cell has a fixed \( E_g \) of approximately 1.1 eV. A high PCE of 28% was achieved in a PVK/CIGS 4-Terminal double junction structure solar cell comprising a PVK top cell and a CIGS bottom cell with \( E_g \) of 1.59 and 1.02 eV, respectively, combined in a spectrum splitting system equipped with a dichroic mirror with splitting wavelengths of 775 nm. As PVK and CIGS are both thin films, tandem devices using these materials can potentially exhibit high flexibilities, which cannot be achieved with Si cells. Spectrum splitting tandem cells may not be ideal for practical applications; however, our study is significantly important because we have shown experimentally that this PVK/CIGS tandem solar cell is not only mechanically superior but also exhibits a higher efficiency compared with Si-based tandem solar cell configurations. These observations will be utilized to design better tandem solar cells in future.

**Limitations of the Study**

In this study, we did not conduct MPP measurement; therefore, the steady-state efficiency may differ from the values presented in the paper to some extent. To compare the PCEs of the spectrum splitting tandem

|                      | PCE (%) | \( J_{sc} \) (mA cm\(^{-2}\)) | \( V_{oc} \) (mV) | FF (%) |
|----------------------|---------|-------------------------------|-------------------|--------|
| PVK-775 nm-Rev.      | 19.1    | 21.0                          | 1,182.0           | 77.2   |
| PVK-775 nm-Frd.      | 18.3    | 20.9                          | 1,172.8           | 74.6   |
| CIGS (\( E_g = 1.14 \) eV) | 7.5    | 14.5                          | 690.9             | 74.9   |
| CIGS (\( E_g = 1.11 \) eV) | 7.9    | 15.3                          | 682.7             | 75.3   |
| CIGS (\( E_g = 1.08 \) eV) | 8.6    | 16.3                          | 678.9             | 77.5   |
| CIGS (\( E_g = 1.02 \) eV) | 8.9    | 18.4                          | 637.0             | 75.8   |
| 4-T tandem (best)    | 28.0    | –                             | –                 | –      |

Table 2. Solar Cell Parameters of the PVK Top Cell and CIGS Bottom Cells Extracted from the J-V Curves and EQE Spectra in Figure 3. The highest 4-T tandem cell efficiency was obtained when the CIGS bottom cell with \( E_g \) of 1.02 eV was used.
devices to other types of tandem devices may not be ideal as most of the optical losses are not taken into consideration for the former; however, the result of this research should provide a guideline for an optimal material design in the fabrication of tandem solar cells in the future.

Resource Availability

Lead Contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Hiroshi Segawa (csegawa@mail.ecc.u-tokyo.ac.jp).

Materials Availability

This study did not generate any new unique reagent.

Data and Code Availability

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

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101817.

ACKNOWLEDGMENTS

A part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO) PV R&D programs.
AUTHORS CONTRIBUTION

M.N. conceived the idea, fabricated the CIGS solar cells, carried out the J-V and EQE measurements, and wrote the manuscript. I.T., Y.K., and Y.H. helped in the CIGS solar cell fabrication. K.T. and C.N. fabricated the perovskite solar cells with support from T.B. T.K. supervised this project. All authors actively took part in the discussion of the results.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: August 27, 2020
Revised: October 21, 2020
Accepted: November 12, 2020
Published: December 18, 2020

REFERENCES

Abdolfahi Nejad, B., Hossain, I.M., Jakoby, M., Moghadamzadeh, S., Abzieher, T., Gharibzadeh, S., Schwenzer, J.A., Nazari, P., Schackmar, F., Hauschild, D., et al. (2020). Vacuum-assisted growth of low-bandgap thin films (FA0.8MA0.2Sn0.5Pb0.5I3) for all-perovskite tandem solar cells. Adv. Energy Mater. 10, 1902583.

Al-Ashouri, A., Magomedov, A., Roß, M., Jo, S., Talakis, M., Chishtikova, G., Bertram, T., Marquez, J.A., Köhnen, E., Kasparavičius, E., et al. (2019). Conformal monolayer contacts with lossless interfaces for perovskite single junction and monolithic tandem solar cells. Energy Environ. Sci. 12, 3356–3369.

Alharbi, F.H., and Kais, S. (2015). Theoretical limits of photovoltaics efficiency and possible improvements by intuitive approaches learned from photosynthesis and quantum coherence. Renew. Sustain. Energy Rev. 43, 1073–1089.

Bar, M., Bohne, W., Rohrich, J., Strub, E., Lindner, S., Xu, T., Fischer, C.H., Nielsen, T.P., and Karg, F. (2004). Determination of the band gap depth profile of the pentenary CuInGaSnS2:Cl chalcopyrite from its composition gradient. J. Appl. Phys. 96, 3857–3860.

Bosi, M., and Pelosi, C. (2007). The potential of III-V semiconductors as terrestrial photovoltaic devices. Prog. Photovolt. Res. Appl. 15, 51–68.

Chen, B., Baek, S., Hou, Y., Aydin, E., De Bastiani, M., Scheffel, B., Proppe, A., Huang, Z., Wei, M., Wang, Y., et al. (2020). Enhanced optical path and reduced oxygen sensitivity. Energy Environ. Sci. 13, 1162–1172.

Duong, T., Pham, H., Kho, T.C., Phang, P., Fong, K.C., Yan, D., Yin, Y., Peng, J., Mahmoud, M.A., Gharibzadeh, S., et al. (2020). High efficiency perovskite-silicon tandem solar cells: effect of surface coating versus bulk incorporation of 2D perovskite. Adv. Energy Mater. 10, 1–15.

Gharibzadeh, S., Hessain, I.M., Fassl, P., Nejad, B.A., Abzieher, T., Schultes, M., Ahlswede, E., Jackson, P., Povalla, M., Schäfer, S., et al. (2020). 2D/3D heterostructure for semitransparent perovskite solar cells with engineered bandgap enables efficiencies exceeding 25% in four-terminal tandems with silicon and CIGS. Adv. Funct. Mater. 1909919.

Green, M.A., Dunlop, E.D., Hohl-Ebinger, J., Yoshida, M., Koppadikas, N., and Hao, X. (2020). Solar cell efficiency tables (version 56). Prog. Photovoltaics Res. Appl. 28, 629–638.

Han, O., Heise, Y.T., Meng, L., Wu, J.-L., Sun, P., Yao, E.-P., Chang, S.-Y., Bae, S.-H., Kato, T., Bermudez, V., et al. (2018). High-performance perovskite/Cu(In,Ga)Se2 monolithic tandem solar cells. Science 361, 904–908.

Hosseinnejad, M. (2019). Enhanced performance of dye-sensitized solar cells using perovskite/DSSCs tandem design. J. Electron. Mater. 48, 5403–5406.

 Jaysankar, M., Paetel, S., Ahlswede, E., Paetzold, U.W., Aernouts, T., Gehlhaar, R., and Poormans, J. (2019). Toward scalable perovskite-based multijunction solar modules. Prog. Photovoltaics Res. 27, 733–738.

 Jaysankar, M., Raul, B.A., Bastos, J., Burgess, C., Weytjens, C., Creatoore, M., Aernouts, T., Kung, Y., Gehlhaar, R., Hadjiport, A., et al. (2019a). Minimizing voltage loss in wide-bandgap perovskites for tandem solar cells. ACS Energy Lett. 4, 259–264.

 Jiang, Y., Feurer, T., Carron, R., Torres-sevilla, G., Moser, T., Pisoni, S., Erni, R., Rossell, M.D., Ochoa, M., Hertwig, R., et al. (2020). High mobility In0.85Ga0.15P: H electrodes for four-terminal perovskite/ CuxSn1-xSe2 tandem solar cells. ACS Nano 14, 7502–7512.

 Kim, D.H., Muzzillo, C.P., Tong, J., Palmstrom, A.F., Larson, B.W., Choi, C., Harvey, S.P., Glynn, S., Whitaker, J.B., Zhang, F., et al. (2019). Bimolecular additives improve wide-band-gap perovskites for efficient tandem solar cells with CIGS. Joule 3, 1734–1745.

 Kinoshita, T., Nonomura, K., Jeon, N.J., Giordano, F., Abate, A., Uchida, S., Kubo, T., Sieck, S. Ii, Nazeeruddin, M.K., Hagfeldt, A., et al. (2015). Spectral splitting photovoltaics with perovskite and wideband dye-sensitized solar cells. Nat. Commun. 6, 1–8.

 Krückmeyer, L., Rau, U., Stolterfoht, M., and Kirchtz, H. (2020). How to report record open-circuit voltages in lead-halide perovskite solar cells. Adv. Energy Mater. 10, 1902573.

Lin, R., Xiao, K., Qin, Z., Han, Q., Zhang, C., Wei, M., Saadatminov, M.I., Gao, Y., Xu, J., Xiao, M., et al. (2019). Monolithic all-perovskite tandem solar cells with 24.8% efficiency exploiting comproportionation to suppress Sn(ii) oxidation in precursor ink. Nat. Energy 4, 864–873.

 Lu, H., Krishna, A., Zakeeruddin, S.M., Grätzel, M., and Hagfeldt, A. (2020). Compositional and interface engineering of organic-inorganic Lead halide perovskite solar cells. Science 329, 1–14.

 Meillaud, F., Shah, A., Droz, C., Vallat-Sauvain, E., and Miazza, C. (2006). Efficiency limits for single-junction and tandem solar cells. Sol. Energy Mater. Sol. Cell 90, 2952–2959.

 Nakamura, M., Yamaguchi, K., Kimoto, Y., Yasaki, Y., Kato, T., and Sugimoto, H. (2019). Cd-free CuIn(Ga)Se2 thin-film solar cell with record efficiency of 23.35%. IEEE J. Photovoltaics 9, 1863–1867.

 Palmstrom, A.F., Eperon, G.E., Leitjens, T., Prassana, R., Habreutinger, S.N., Nemeth, W., Gaulding, E.A., Dunfield, S.P., Reese, M., Nanayakkara, S., et al. (2019). Enabling flexible all-perovskite tandem solar cells. Joule 3, 2193–2204.

 Peters, I.M., Rodriguez Gallegos, C.D., Soña, S.E., and Buonassisi, T. (2019). The value of efficiency in photovoltaics. Joule 3, 2732–2747.

 Shen, H., Duong, T., Peng, J., Jacobs, D., Wu, N., Gong, J., Wu, Y., Karuturi, S.K., Fu, X., Weber, K., et al. (2018). Mechanically-stacked perovskite/ CIGS tandem solar cells with efficiency of 23.9% and reduced oxygen sensitivity. Energy Environ. Sci. 11, 394–406.

 Shockley, W., and Queisser, H.J. (1961). Detailed balance limit of efficiency of p-n junction solar cells. J. Appl. Phys. 32, 510–519.

 Tang, Z., Bessho, T., Arai, F., Kinoshita, T., Maitani, M.M., Jono, R., Murakami, T.N., Wang, H., Kubo, T., Uchida, S., et al. (2017). Hysteresis-free perovskite solar cells made of potassium-doped organometal halide perovskite. Sci. Rep. 7, 12183.

 Tong, J., Song, Z., Kim, D.H., Chen, X., Chen, C., Palmstrom, A.F., Niidome, P.F., Reese, M.O., Dunfield, S.P., Reid, O.G., et al. (2019). Carrier lifetimes of >1 us in Sn-Pb perovskites enable
efficient all-perovskite tandem solar cells. Science 364, 475–479.

De Vos, A. (1980). Detailed balance limit of the efficiency of tandem solar cells. J. Phys. D. Appl. Phys. 13, 839–846.

Uzu, H., Ichikawa, M., Hino, M., Nakano, K., Meguro, T., Hernández, J.L., Kim, H.S., Park, N.G., and Yamamoto, K. (2015). High efficiency solar cells combining a perovskite and a silicon heterojunction solar cells via an optical splitting system. Appl. Phys. Lett. 106, 013506.

Wang, Z., Zhu, X., Zuo, S., Chen, M., Zhang, C., Wang, C., Ren, X., Yang, Z., Liu, Z., Xu, X., et al. (2020). 27%-Efficiency four-terminal perovskite/silicon tandem solar cells by sandwiched gold nanomesh. Adv. Funct. Mater. 30, 1–8.

Xu, J., Boyd, C.C., Yu, Z.J., Palmstrom, A.F., Witter, D.J., Larson, B.W., France, R.M., Werner, J., Harvey, S.P., Wolf, E.J., et al. (2020). Triple-halide wide-band gap perovskites with suppressed phase segregation for efficient tandems. Science 367, 1097–1104.

Yang, Z., Yu, Z., Wei, H., Xiao, X., Ni, Z., Chen, B., Deng, Y., Haberreutinger, S.N., Chen, X., Wang, K., et al. (2019). Enhancing electron diffusion length in narrow-bandgap perovskites for efficient monolithic perovskite tandem solar cells. Nat. Commun. 10, 4498.

Yao, Y., Lv, F., Luo, L., Liao, L., Wang, G., Liu, D., Xu, C., Zhou, G., Zhao, X., and Song, Q. (2020). Highly efficient Sn-Pb perovskite solar cell and high-performance all-perovskite four-terminal tandem solar cell. Sol. RRL 4, 1900396.

Zhao, D., Wang, C., Song, Z., Yu, Y., Chen, C., Zhao, X., Zhu, K., and Yan, Y. (2018). Four-terminal all-perovskite tandem solar cells achieving power conversion efficiencies exceeding 23%. ACS Energy Lett. 3, 305–306.
Supplemental Information

Perovskite/CIGS Spectral Splitting
Double Junction Solar Cell with 28%
Power Conversion Efficiency

Motoshi Nakamura, Keishi Tada, Takumi Kinoshita, Takeru Bessho, Chie Nishiyama, Issei Takenaka, Yoshinori Kimoto, Yuta Higashino, Hiroki Sugimoto, and Hiroshi Segawa
SUPPLEMENTAL INFORMATION

Transparent Methods

Materials:
All chemicals were used as-purchased without any purification. Titanium diisopropoxide bis (acetylacetonate) (75 wt.% in isopropanol) and lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) were obtained from Sigma-Aldrich. Bis (trifluoromethanesulfonyl) imide (Mg(TFSI)₂) and 4-tert-butylpyridine (tBP) were purchased from Tokyo Chemical Industry (TCI) Co., LTD. 24-nm TiO₂ paste (PST-24NR) was purchased from JGC C&C®. The materials for the perovskite absorber preparation, including PbBr₂ (99%), KI (>99.5%), and Magnesium(II) were also obtained from TCI Co., LTD FAI (>99%), MABr (>98%) was purchased from GreatCell Solar Limited, and PbI₂ (99.99%) was purchased from Kojundo Chemical Laboratory Co., LTD. Spiro-OMeTAD (>99.97%) was purchased from Nippon Fine Chemical Co., LTD. Solvents were purchased from Wako Pure Chemical Industries, LTD and Sigma-Aldrich Co. LTD. Mo target (>99.9%), Cu-Ga target (>99.99%), and In target (>99.99%) were obtained from PLANSEE Japan Ltd., Mitsubishi Materials Corporation, and IX Nippon Mining & Metals Corporation, respectively. H₂Se and H₂S gases were purchased from Tomoe Shokai Co., Ltd.

Perovskite Solar Cell Fabrication:
FTO glass with an anti-reflective coating from GEOMATEC Co., Ltd. was employed as a transparent conductive substrate. The substrate was ultrasonically cleaned with acetone and methanol sequentially, and UV-Ozone cleaning was performed for the FTO surface. The compact TiO₂ (c-TiO₂) layer, mesoporous TiO₂ (m-TiO₂) layer, PVK layer, Spiro-OMeTAD layer, and Au layer were sequentially deposited. More specifically, the c-TiO₂ layer was deposited by a spray pyrolysis method from a titanium diisopropoxide bis (acetylacetonate) precursor solution containing LiTFSI and Mg(TFSI)₂ in dehydrated ethanol. The m-TiO₂ layer was formed by the spin coating method with a diluted PST-24NR in dehydrated ethanol suspension followed by the Li-doping with LiTFSI containing solution (0.1 M) in acetonitrile. The perovskite precursor solution containing 1.15 M PbI₂, 0.20 M PbBr₂, 0.20 M MABr, and 1.09 M FAI was prepared by dissolving all the powders in DMF and DMSO mixed solvent with a volume ratio of 4:1, and separately prepared 0.05 M KI in DMSO was added to the previous solution. The PVK layer was formed via an anti-solvent method with chlorobenzene. Then, LiTFSI and tBP doped Spiro-OMeTAD (60 mM) was spin-casted as the hole transport layer followed by 80 nm-thick Au electrode deposition by thermal evaporation.

CIGS Solar Cell Fabrication:
A cleaned glass substrate was placed in an in-line DC-magnetron sputtering system, where a Mo back electrode and CuGa/In metal precursors with a certain amount of additives such as Na were sequentially deposited. Then, the substrates were placed in a rapid thermal annealing (RTA) furnace for the sulfurization after selenization (SAS) process, where the precursor layers turned into CIGS absorber layers. CIGS absorber layers with various E_g were prepared by tuning some of the SAS process parameters such as temperature. The absorber layers then underwent the Cs treatment for the surface passivation. Zn(O,S,OH)_x/Zn_0.8Mg_0.2O double layers deposited by a combination of chemical bath deposition and atomic layer deposition techniques were used as the buffer layer. Next, ZnO:B was deposited as a transparent conductive layer by a metal-organic chemical-vapor deposition. Finally, 20 µm of Al and 120 nm of MgF₂ were deposited as the grid electrode and anti-reflective layer, respectively, using the electron beam evaporation method.

Device Characterization:
The current density–voltage (J–V) characteristics of the cells were measured with a class AAA solar simulator, WXS-350S-L2MS (Wacom) under the standard test conditions (AM1.5G, 1000 W/m², 25 °C). Light intensity was calculated using a Si photodiode, BS-500BK (Bunkokeiki). EQE values were measured with a YQ-M11 instrument (Bunkoukeiki). Dichroic mirrors from Semrock® were used as the spectrum splitter.
Figure S1. Calculated theoretical efficiency limit of 2 terminal (2-T) and 4 terminal (4-T) double junction solar cells plotted as a function of top and bottom cell bandgaps and schematics of different terminal architectures of the devices: (a) 2-T monolithic, (b) 2-T mechanical stack, (c) 4-T mechanical stack, and (d) 4-T spectrum splitting. The calculation is based on the detailed balance theory (Shockley et al., 1961) and an assumption that every single photons with lower energy than top cell $E_g$ reaches the bottom cell. Related to Figure 1.
Figure S2. Elemental and $E_g$ Depth profiles of CIGS absorbers used in this report: (a) \([\text{Ga}]/(\text{[Ga]}+\text{[In]}]\), (b) \([\text{S}]/(\text{[S]}+\text{[Se]}]\), (c) $E_g$. Related to Figure 2.
Figure S3. Relation between the solar cell device parameters of CIGS bottom cell with different bandgaps (1.02 and 1.14 eV) as a function of the splitting wavelength of the dichroic mirror. Related to Figure 3.
Table S1. Reported high PCE of perovskite-based double junction solar cells in order of the area by bottom cell distinction. One square centimeter devices are shown in a bold-face. Related to Table 2.

| Article                      | Tandem Architecture | Top cell | Bottom cell | Area (cm²) | PCE (%) |
|------------------------------|---------------------|----------|-------------|------------|---------|
| Chen et al., 2020            | 4-T mechanical      | [Cs,FA,MA]Pb[I,Br]₃, Si | 0.05        | 28.6      |
| Uzu et al., 2015             | 4-T splitting       | MAPbI₃   | Si          | 0.20       | 28.0    |
| Duong et al., 2020           | 4-T mechanical      | [Rb,Cs,FA,MA]Pb[I,Br]₃, Si | 0.21        | 27.7      |
| Xu et al., 2020              | 2-T monolithic      | [Cs,FA,MA]Pb[I,Br,Cl]₃, Si | 1.00        | 27.1      |
| Jaysankar et al., 2019a      | 4-T mechanical      | [Cs,FA]Pb[I,Br]₃, Si | 0.13        | 27.1      |
| Wang et al., 2020            | 4-T mechanical      | MAPbI₃   | Si          | 0.10       | 27.0    |
| **This work**                | **4-T splitting**   | [K,FA,MA]Pb[I,Br]₃, CIGS | **1.00**    | **28.0**  |
| Kim et al., 2019             | 4-T mechanical      | [Cs,FA,MA]Pb[I,Br]₃, CIGS | 0.06        | 25.9      |
| Gharibzadeh et al., 2020     | 4-T mechanical      | [Cs,FA]Pb[I,Br]₃, CIGS | 0.11        | 25.0      |
| Shen et al., 2018            | 4-T mechanical      | [K,Cs,FA,MA]Pb[I,Br,Cl]₃, CIGS | 0.30        | 24.6      |
| Jiang et al., 2020           | 4-T mechanical      | [RbCsFAMA]Pb[I,Br]₃, CIGS | 0.30        | 23.9      |
| Jaysankar et al., 2019b      | 4-T mechanical      | [Cs,FA]Pb[I,Br]₃, CIGS | 0.13        | 23.8      |
| Al-Ashouri et al., 2019      | 2-T monolithic      | [Cs,FA,MA]Pb[I,Br]₃, CIGS | 1.00        | 23.3      |
| Han et al., 2018             | 2-T monolithic      | [Cs,FA,MA]Pb[I,Br]₃, CIGS | 0.04        | 22.4      |
| Tong et al., 2019            | 4-T mechanical      | [Cs,FA,MA]Pb[I,Br]₃, PVK | 0.11        | 25.0      |
| Lin et al., 2019             | 2-T monolithic      | [Cs,FA]Pb[I,Br]₃, PVK | 0.05        | 24.8      |
| Palmstrom et al., 2019       | 4-T splitting       | MAPb[I,Cl]₃, PVK | 0.06        | 23.3      |
| Zhao et al., 2018            | 4-T mechanical      | [Cs,FA]Pb[I,Br]₃, PVK | 0.1         | 23.1      |
| Yao et al., 2020             | 2-T monolithic      | [Cs,FA,MA]Pb[I,Br]₃, PVK | 0.06        | 23.1      |
| Abdollahi et al., 2020       | 4-T mechanical      | [Cs,FA,MA]Pb[I,Br]₃, PVK | 0.11        | 23.0      |
| Yang et al., 2019            | 2-T monolithic      | [Cs,FA]Pb[I,Br]₃, PVK | 0.08        | 23.0      |
| Kinoshita et al., 2015       | 4-T splitting       | [FA,MA]Pb[I,Br]₃, DS | 0.16        | 21.5      |

References
Shockley, W., and Queisser, H.J. (1961). Detailed Balance Limit of Efficiency of p‐n Junction Solar Cells. J. Appl. Phys. 32, 510–519.