# Pb-free perovskite solar cells composed of Sn/Ge(1:1) alloyed perovskite layer prepared by spin-coating

*Huan Bi*, Mengmeng Chen, Liang Wang, Zheng Zhang, Chao Ding, Gaurav Kapil, Shahrir Razey Sahamir, Yoshitaka Sanehira, Ajay Kumar Baranwal, Takeshi Kitamura, Guozheng Shi, Qing Shen*, and Shuzi Hayase**

Faculty of Informatics and Engineering, The University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan.

**Corresponding Authors (H. Bi, Q. Shen, S. Hayase)**

E-mail:

hbi.trans.sci@uec.ac.jp;

shen@pc.uec.ac.jp;

hayase@uec.ac.jp.

*Materials:* Tin(II) iodide ($SnI_2$, 99.99%), germanium (II) iodide ($GeI_2$, >99.8%), N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene (CB), n-pyrrolidinone (NMP) were purchased from Sigma-Aldrich. Methylamine Hydroiodide (MAI, Low water content, >99.0%) was purchased from Tokyo Chemical Industry Co., Ltd. Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT: PSS) was obtained from CLEVIOS PVP AI 4083.

*Device Fabrication:* The glass was cleaned with water, acetone, and isopropanol sequentially for 15 min. Then, the FTO was dried, followed by being treated with plasma for 5 min. PEDOT: PSS as hole transport layer was spin-coated on the FTO with 5000 rpm for the 50s. After that, the substrate was annealed at 180°C for 20 min. Then the substrate was transferred and kept in the $N_2$-filled glovebox. For the $MASn_xGe_{1-x}I_3$ perovskite solution, 1M $MASnI_3$ (Sn 1soln) was prepared by mixing 1M MAI and 1M $SnI_2$ in DMF. In the same way, 1M $MAGeI_3$ solution (Ge 1soln) was obtained by dissolving 1M MAI and 1M $GeI_2$ in DMF: NMP (v: v=4:1). They were stirred for 3 hours at room temperature inside the glove box, separately. 1M $MASn_{0.5}Ge_{0.5}I_3$ ($Sn_{0.5}Ge_{0.5}$ Non) was prepared from the Ge 1soln and Sn 1soln (1:1 mol). The perovskite layer of Device 1 was prepared as follows: 100 μL of DMSO was added to the 1 mL Sn/Ge 1soln and the mixed solution ($Sn_{0.5}Ge_{0.5}$ DMSO solution) was spin-coated, followed by an anti-solvent process, where 500 μL of chlorobenzene (CB) was dropped on the film at 15s after the program started. Then, the film was annealed at 70 ºC for 20 min. The perovskite layer of the Device 2 was prepared as follows: 50 μL of the mixture of (TEA: DMF=1:50 (v: v)) was added into Sn0.5Ge0.5 Non. The mixed solution ($Sn_{0.5}Ge_{0.5}$ TEA solution) was spin-coated on the PEDOP-PSS layer. The film was dried at room temperature. On each perovskite layer, fullerene (C60: 20nm), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP: 7 nm), and Ag (100 nm) were deposited to complete each device.

*Characterization:* The solar cell performances were measured by using a Keithley 4200 source meter and a solar simulator under 100mW $cm^{-2}$ AM 1.5G (Bunkouki CEP-2000SRR). The espoused area was fixed to 0.1 $cm^2$ using a non-reflective black metal mask. The EQE spectra were recorded using a monochromatic Xenon lamp (Bunkouki CEP-2000SRR). The EQE measurement was carried out under monochromatic light from 1200 to 300 nm (300W Xenon lamp with a monochromator, Newport 74010). The crystal structure was measured by the XRD (Rigaku Smartlab XRD) with monochromatic Cu $K_\beta$ irradiation (45 kV 200 mA). The bandgap of the film was estimated via the UV-Vis (JASCO V-670). XPS spectra were collected by Shimadzu Kratos Axis-Nova spectrometer. Mg $K_\alpha$ excitation source was used at pass energy of 80 eV and the energy resolution was 1000 meV. PYS was measured using the Bunkoukeiki KV 205-HK ionization energy system with the applied voltaic of -10 V.

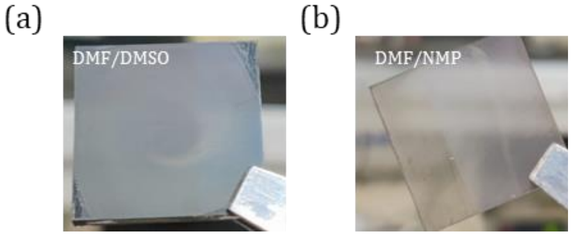

Fig. S1 $MASn_{0.5}Ge_{0.5}I_3$ perovskite film prepared with the solution of (a) DMF/DMSO (4:1) and (b) DMF/NMP (4:1).

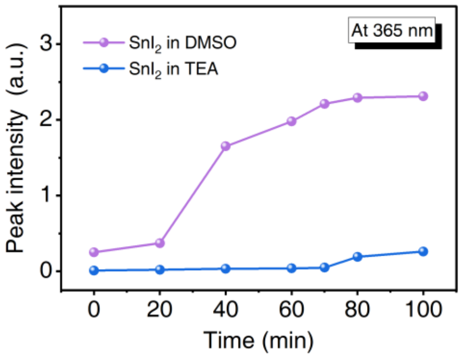

Fig. S2 Change of SnI$_2$ peak intensity in DMSO solution or TEA solution (DMSO solution: DMF:NMP:DMSO=4:1:0.5, volume; TEA solution: DMF:NMP:TEA=4:1:0.25, volume). The results were obtained from Fig. 1a-b.

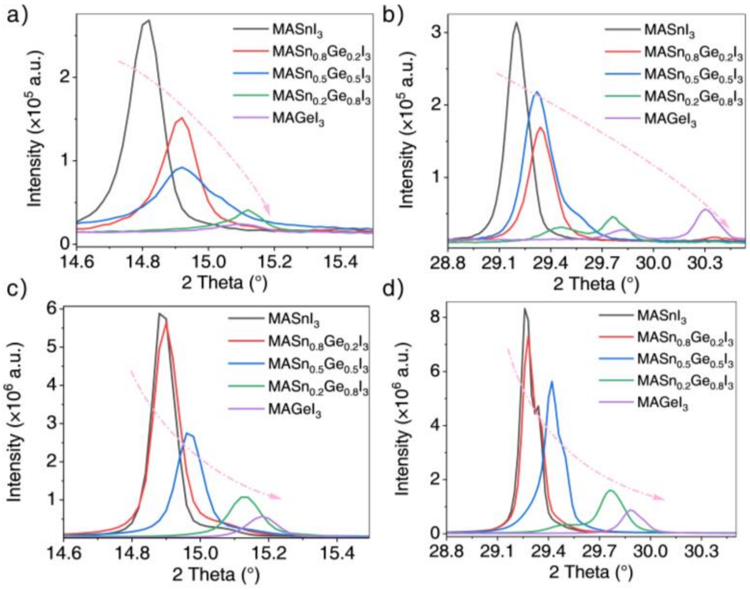

Fig. S3 (a-b) and (c-d) shows the partial enlarged view of Fig. 2a and Fig. 2b, respectively. It can be seen that with the increase of $Ge^{2+}$, the XRD peak position of the film gradually increases.

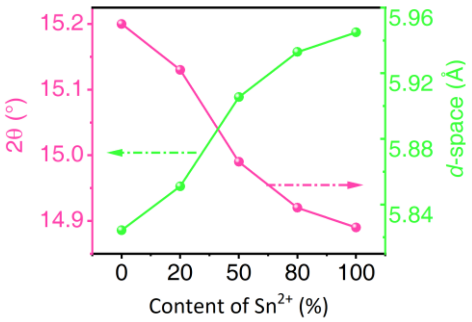

Fig. S4 (001) crystal plane peak position and *d*-space of $MASn_xGe_{1-x}I_3$ when *x* was changed.

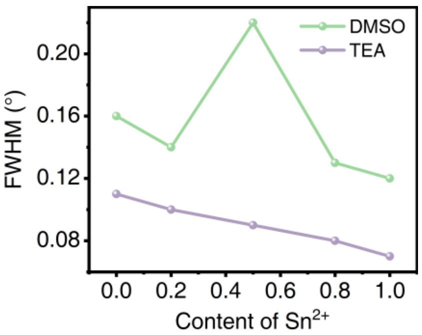

Fig. S5 Statistics of $MASn_xGe_{1-x}I_3$ FWHM in Fig. S3a and Fig. S3c.

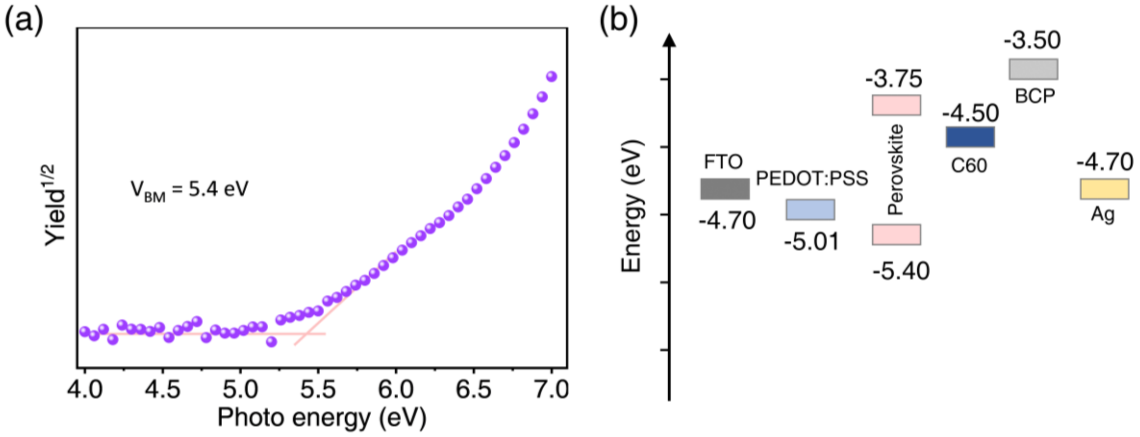

Fig. S6 (a) PYS spectra of $MASn_{0.5}Ge_{0.5}I_3$ perovskite films and (b) Energy level of each layer used in this work.

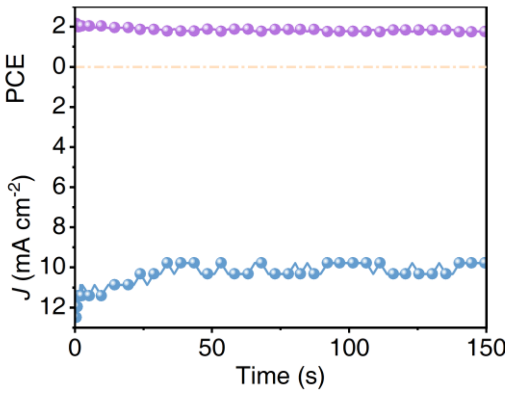

Fig. S7 Steady-state current density and PCE versus time for the best-performing devices employing $MASn_{0.5}Ge_{0.5}I_3$ solar cell (Device 2) prepared from TEA solution. These were measured at the maximum power point.

**Table S1.** Photovoltaic parameters of best-devices prepared from various solution. They were measured in reverse and forward scans under AM 1.5G with one sun illumination of 100 mW/cm$^2$.

| Devices | Sweep | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | PCE (%) |
|---|---|---|---|---|---|
| Device 1 | RS | 10.15 | 0.280 | 0.480 | 1.36 |
| | FS | 9.25 | 0.260 | 0.47 | 1.13 |
| Device 2 | RS | 11.04 | 0.380 | 0.530 | 2.18 |
| | FS | 10.09 | 0.360 | 0.500 | 1.81 |
| Device 3 | RS/FS | | | | |
| Device 4 | RS/FS | | | | |

Device 1 Prepared from DMF/NMP/DMSO (4:1:0.5) with antisovent

Device 2 Prepared from DMF/NMP/TEA (4:1:0.25) without anti-solvent

Device 3 Prepared from DMF/DMSO (4:1) with antisolvent

Device 4 Prepared from DMF/DMSO (4:1) with antisolvent