Mixed Sn-Ge Perovskite for Enhanced Perovskite Solar Cell Performance in Air

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Methods

Materials

All materials were used without any purification. Tin (II) iodide (SnI$_2$, 99.99 %, Sigma Aldrich), tin (II) fluoride (SnF$_2$, 99 %, Sigma Aldrich), formamidinium iodide (FAI, >98.0 %, TCI), methylammonium iodide (MAI, >98.0 %, TCI), germanium (II) iodide (GeI$_2$, >99.8 %, Sigma Aldrich), PEDOT-PSS (Clevious PVP AI 4083), N,N-dimethylformamide (DMF, 99.8%, Sigma Aldrich), dimethyl sulfoxide (DMSO, ≥99.9%, Sigma Aldrich).

Perovskite film preparation

The FA$_{0.75}$MA$_{0.25}$SnI$_3$ precursor solution was prepared by dissolving SnI$_2$ (596 mg), SnF$_2$ (25 mg) and FAI (206 mg), MAI (64 mg) in DMF (1773 µl) and DMSO (227 µl). The FA$_{0.75}$MA$_{0.25}$GeI$_3$ precursor solution was prepared by dissolving GeI$_2$ (131 mg), FAI (52 mg) and MAI (16 mg) in DMF (500 µl). The FA$_{0.75}$MA$_{0.25}$Sn$_{1-x}$Ge$_x$I$_3$ mixed halide perovskite solution was prepared by mixing the FA$_{0.75}$MA$_{0.25}$SnI$_3$ and FA$_{0.75}$MA$_{0.25}$GeI$_3$ solution at a volume ratio of x: (1- x). Before mixing, both precursor solutions were filtered using a 0.20 µm PTFE filter. The solutions were prepared in a nitrogen-purged glovebox.

Device fabrication

The ITO glass substrates were cleaned in detergent, deionized water, acetone and isopropyl alcohol in an ultrasonic bath for 15 mins in each solution. The cleaned ITO substrates were cleaned with oxygen plasma for 5 min before spin-coating with PEDOT-PSS (filtered with 0.45 µm PVDF filter). The PEDOT-PSS layer was spin-coated at 5000 r.p.m for 50 s and then annealed at 140 ºC for 20 min. The solution was spin-coated on the substrate at 5000 r.p.m for 50

s with toluene used as the anti-solvent. All the perovskite films were annealed on a hotplate at 70 $^{\circ}$C for 10 min. Subsequently, C_{60} (50 nm), BCP (8 nm), Ag (70 nm) and Au (10 nm) were sequentially evaporated by thermal evaporation under vacuum resulting in an active area of 0.405 cm^2.

Characterizations

The XRD patterns were obtained by a Rigaku Smartlab X-ray diffractometer with monochromatic Cu-Kβ irradiation (45 kV/200 mA). The UV-Vis measurement was performed using a JASCO V-670 Spectrophotometer. Photoacoustic measurement was performed using a gas-microphone photoacoustic (PA) technique with a 300 W Xenon arc lamp was used as a light source. The wavelength used was 500 – 1200 nm with a modulation frequency of 33 Hz. Photoelectron yield spectroscopy (PYS) was used to determine the valence band using a Bunkoukeiki KV205-HK ionization energy measurement system with – 5.0 V of applied voltage. The atomic force microscopy images were obtained using a scanning probe microscope (JSPM-5200). X-ray Photoelectron Spectroscopy (XPS) analysis was performed using Shimadzu Kratos Axis-Nova spectrometer. Al Kα excitation source was used at a pass energy of 80 eV and the energy resolution was 1000 meV. The thickness of the film was measured using a 3D surface profile measurement system (Nikon BW-A501). The solar cell measurement was performed using a Keithley 4200 source meter and a solar simulator under 100 mW cm^{-2} AM 1.5G in air (Bunkouki CEP-2000SRR). The measured area was fixed to be 0.1 cm^2 non-reflective metal mask. The IPCE spectra were recorded using a monochromatic Xenon lamp (Bunkouki CEP-2000SRR).
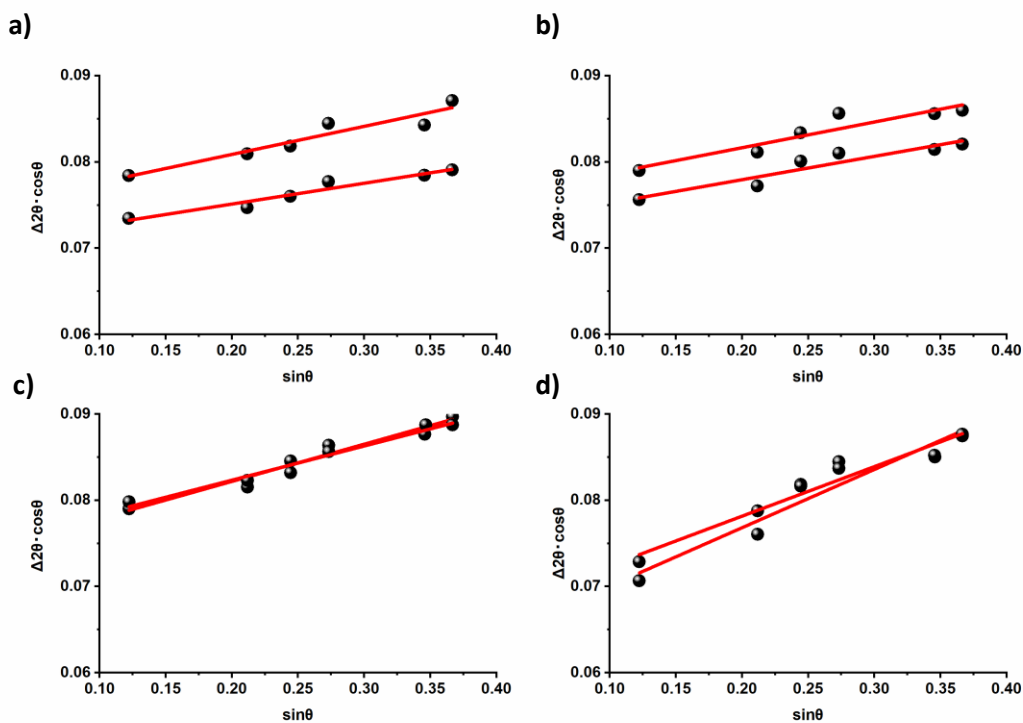
Figure S1 Williamson-Hall plot of a) x=0, b) x=0.05, c) x=0.10 and d) x=0.20 using data obtained from XRD

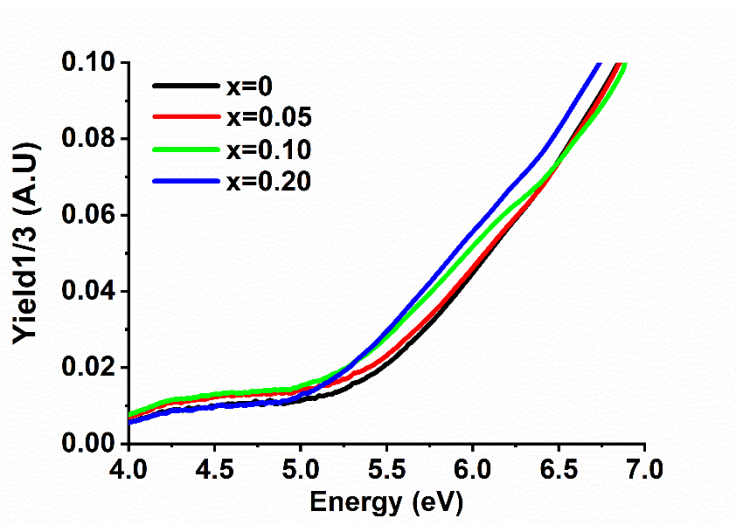diffraction pattern. For each type of material, two samples were prepared for XRD characterization.

Figure S2 Photoelectron yield spectroscopy of the prepared perovskite materials measured on ITO
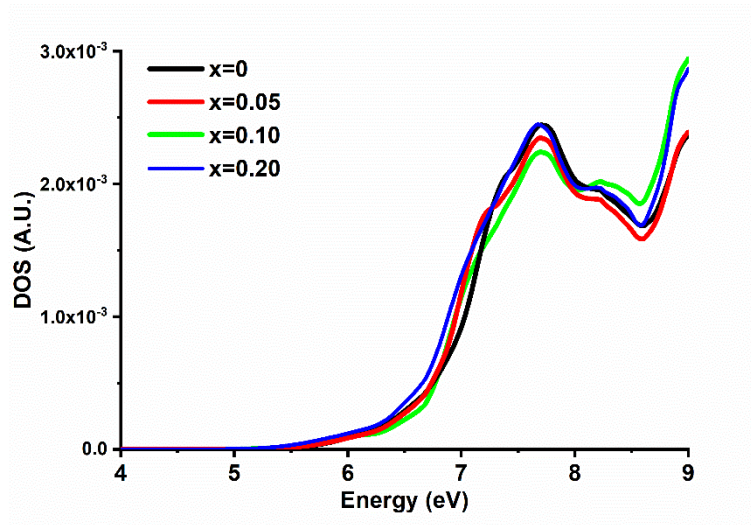
substrates under vacuum (10^{-4} Pa).

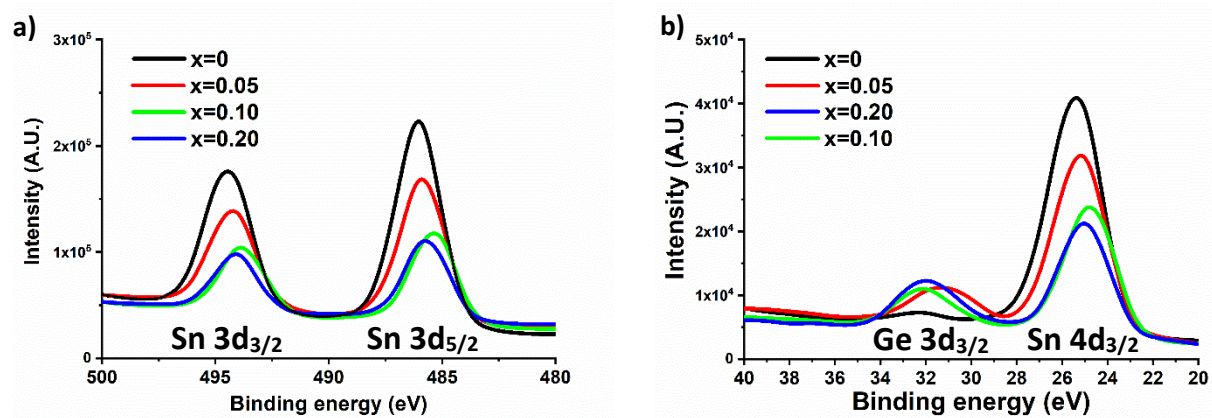Figure S3 Plot of density of states as a function of energy.

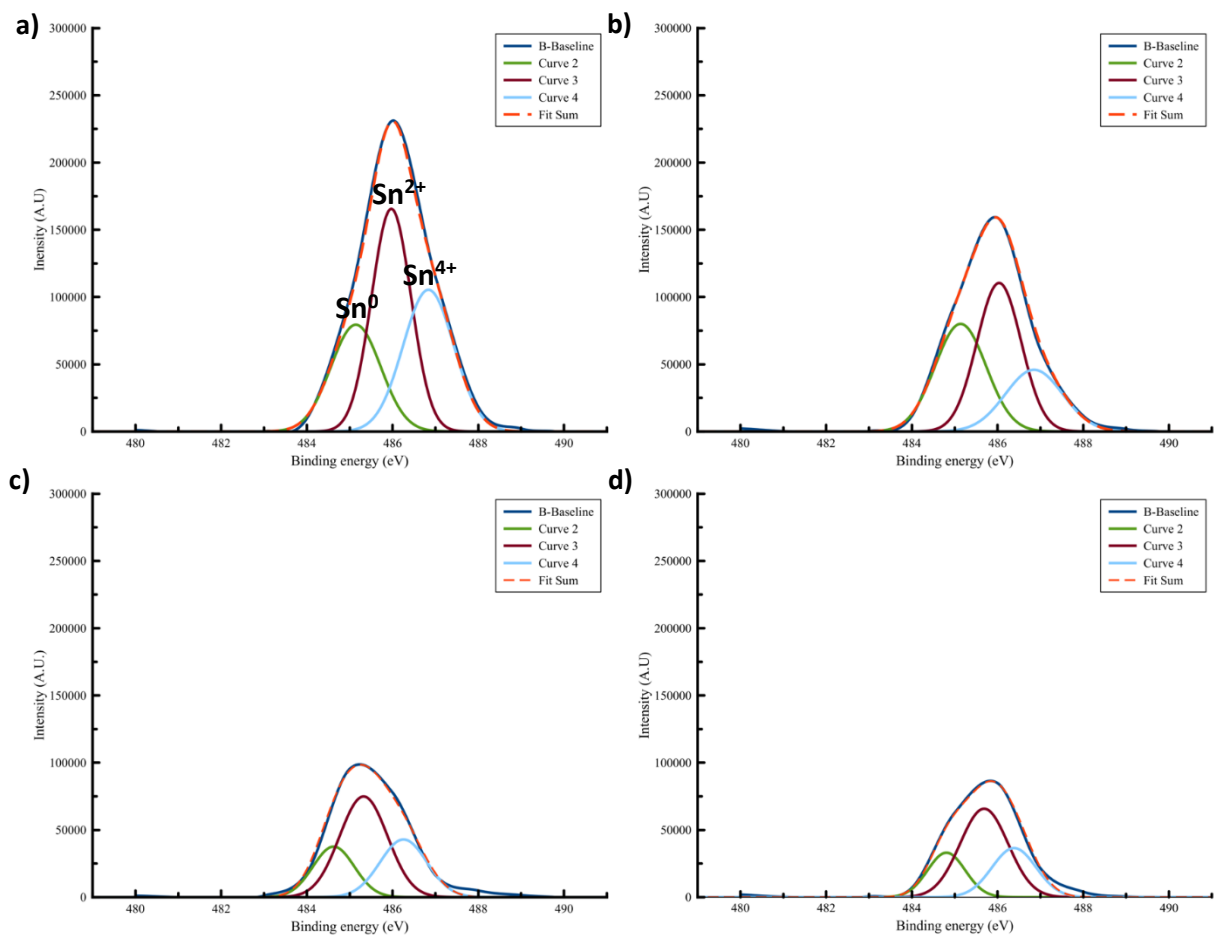Figure S4 XPS peaks for a) Sn $3d_{3/2}$ and Sn $3d_{5/2}$, and b) Ge $3d_{3/2}$ and Sn $4d_{3/2}$.

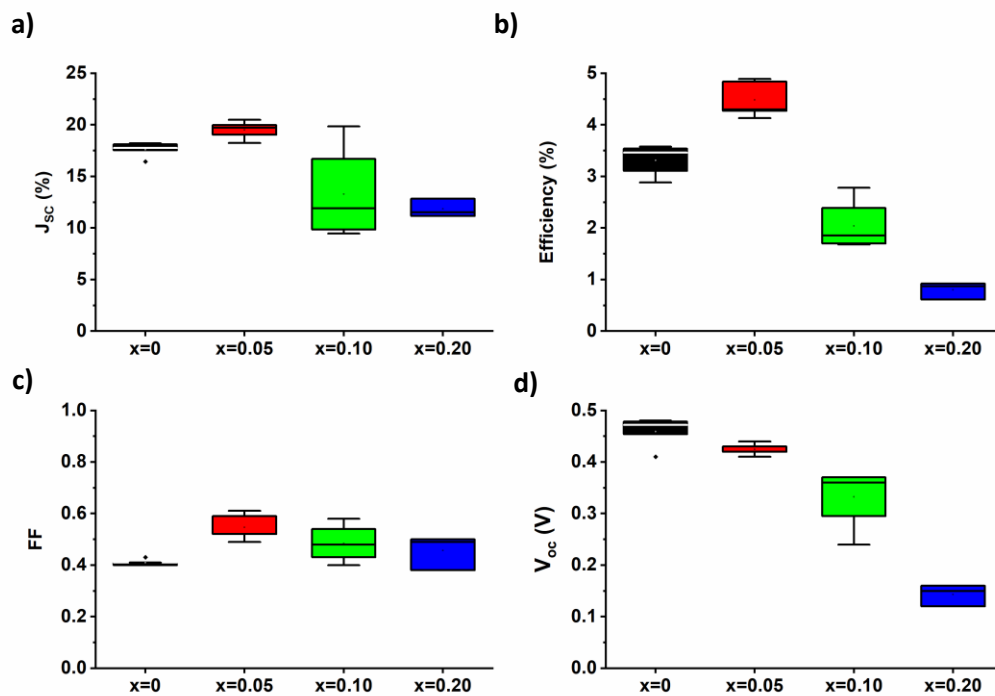Figure S5 XPS spectra for Sn signal fitted using Gaussian fit. a) x=0, b) x=0.05, c) x=0.10 and d) x=0.20.

Figure S6 Photovoltaic parameters for the solar cells with different germanium content. a) J_{SC}, b) power conversion efficiency, c) fill factor and d) V_{OC}.

Table S1 Summary of XPS intensity of Sn^{4+} as a function of Ge content. The value is normalized against that of X=0 sample.

Sample	Normalized intensity of Sn^{4+}
X=0	1.00
X=0.05	0.44
X=0.10	0.41
X=0.20	0.35