Supporting information

Impact of cation substitution in all solution-processed $Cu_2(Cd,Zn)SnS_4$ superstrate solar cells

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Table S1. Material properties used for the calculation of the bands.

	CZTS	CCTS	CdS	ZnS	TiO_2	FTO
Thickness (nm)	600	600	50	50	150	150
Dielectric constant ($\varepsilon_0/ \varepsilon$)	7	7	10	9	30	9
E_g (eV)	1.5	1.4	2.42	3.6	3.2	3.8
Electron affinity (eV)	4.2	4.47	4.4	3.5	4	4.1
N_c/N_v	0.0255	0.0255	0.0112	0.044	50	1.2
n_i (cm^{-3})	$1.8\ 10^{6}$	$2.3\ 10^{9}$	0.182	0.01	$1.44\ 10^{-5}$	$3.6\ 10^{-13}$
Doping concentration (cm^{-3})	10^{16}-10^{18}	10^{16}	10^{17}	10^{18}	10^{17}	$2\ 10^{19}$
References	[1–3]	[1]	[1,3,4]	[3,4]	[5]	[5]

Table S2. Compositional ratios of CCZTS thin films.

	Cd/(Cd+Zn)	Cu/(Cd+Zn+Sn)	(Cd+Zn)/Sn	S/Metals
Stoichiometry	-	1	1	1
Precursor solution	x	0.8	0.8	5
CZTS	0.00	0.79	1.24	0.91
x=0	0.35	0.64	1.98	1.00
x=0.25	0.53	0.64	2.02	1.07
x=0.5	0.63	0.63	2.00	1.03
x=0.75	0.82	0.78	1.94	1.07
x=1	1.00	0.75	1.57	1.04

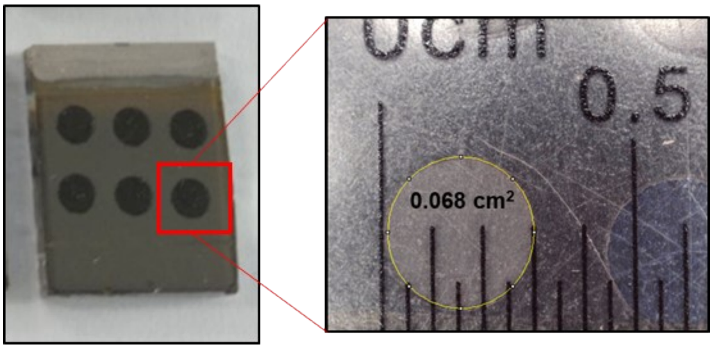

Figure S1. A microscope image of a carbon dot electrode, which defines the cell area.

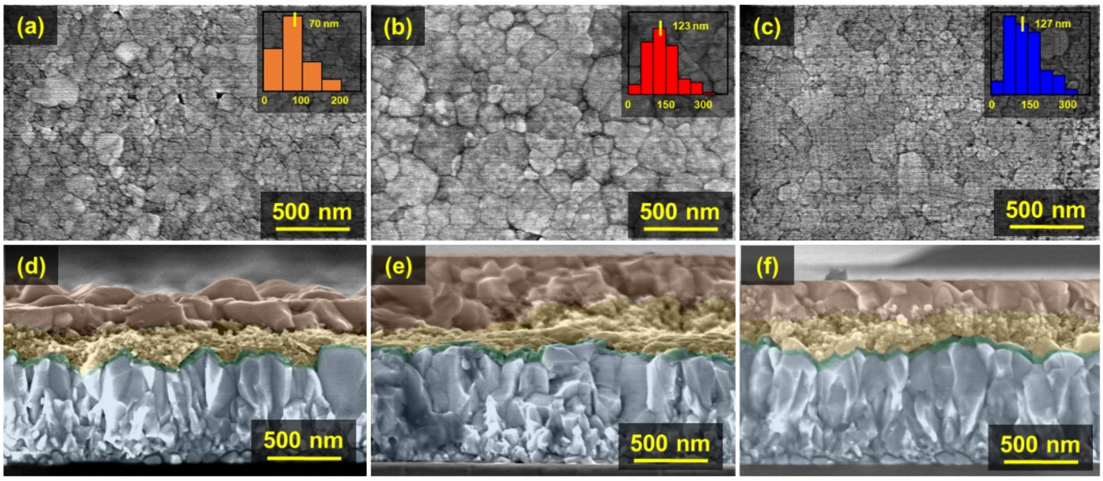

Figure S2. SEM top and cross-sectional view of the samples a), d) CZTS, b), e) x = 0.25 and c), f) x = 0.5 respectively. In the inset, a histogram distribution and average of the grain size. The films are marked as blue (FTO), green (planar TiO_2), yellow (mesoporous TiO_2 + (Cd,Zn)S), and red (CCZTS).

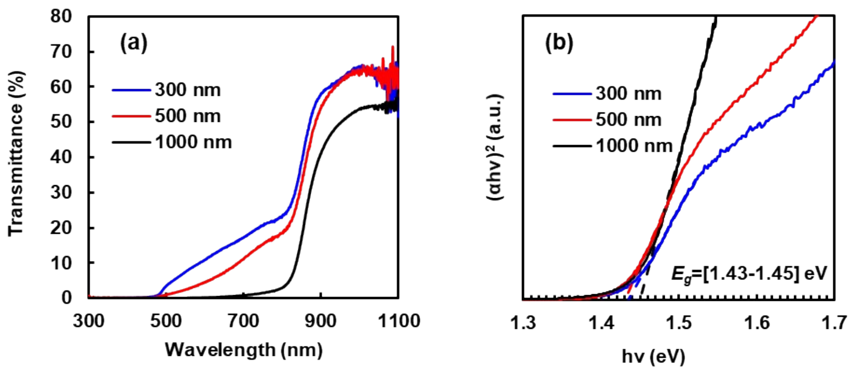

Figure S3. a) Transmittance spectra, and b) Tauc plot with band gap calculation of samples with different absorber thickness, prepared with an x=0.75 solution.

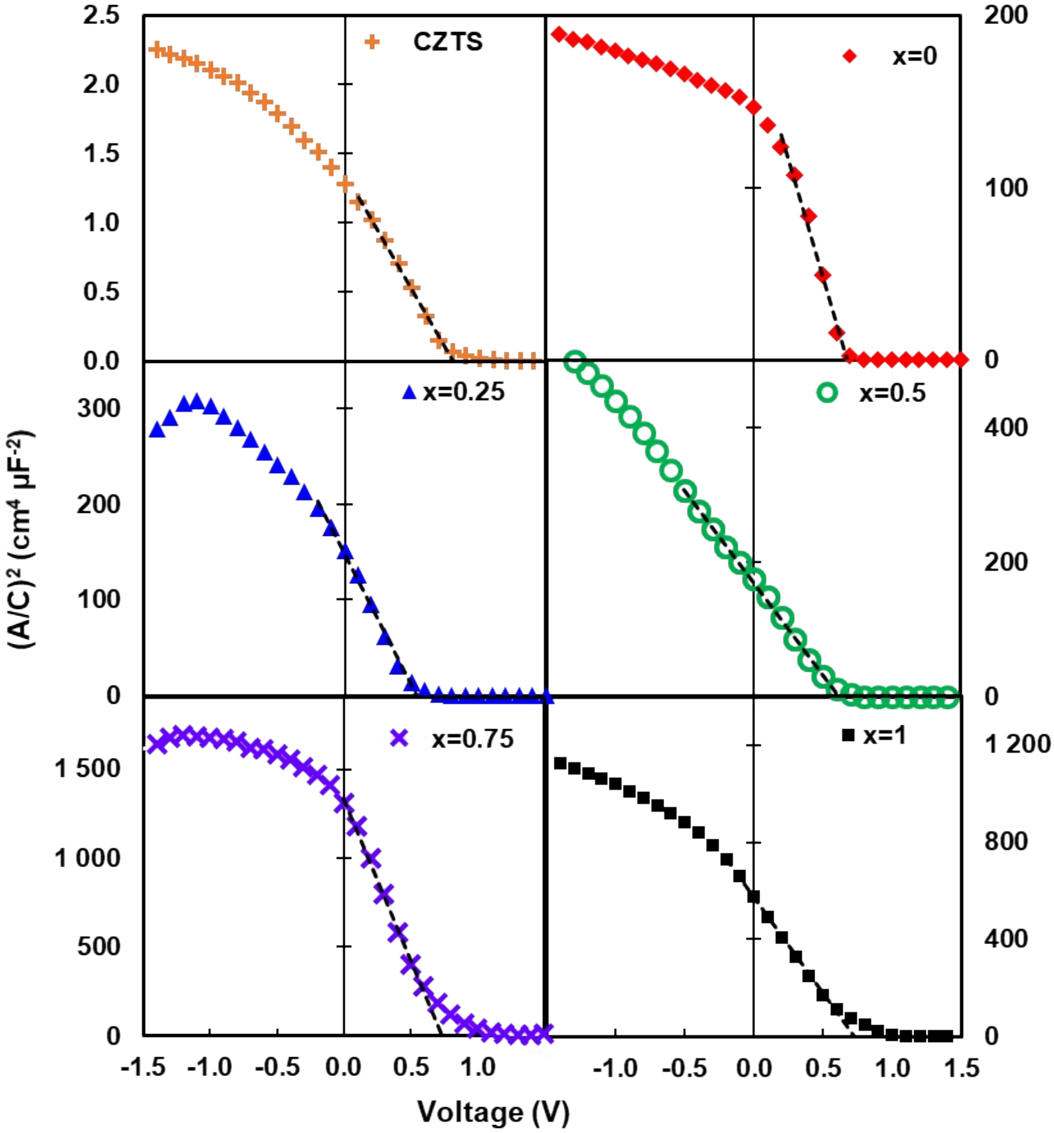

Figure S4. Mott-Schottky plots with a linear regression were used to calculate the built-in potential. The measurements were obtained under dark, using a 20 mV AC at 100 kHz.

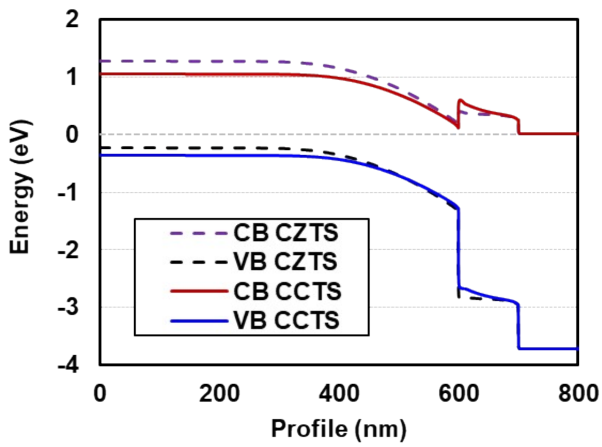

Figure S5. Junction formed between the absorber layer and TiO_2. It consists of a spike-like junction, with a small barrier for CZTS than CCTS (both with doping of 10^{16} cm^{-3}).

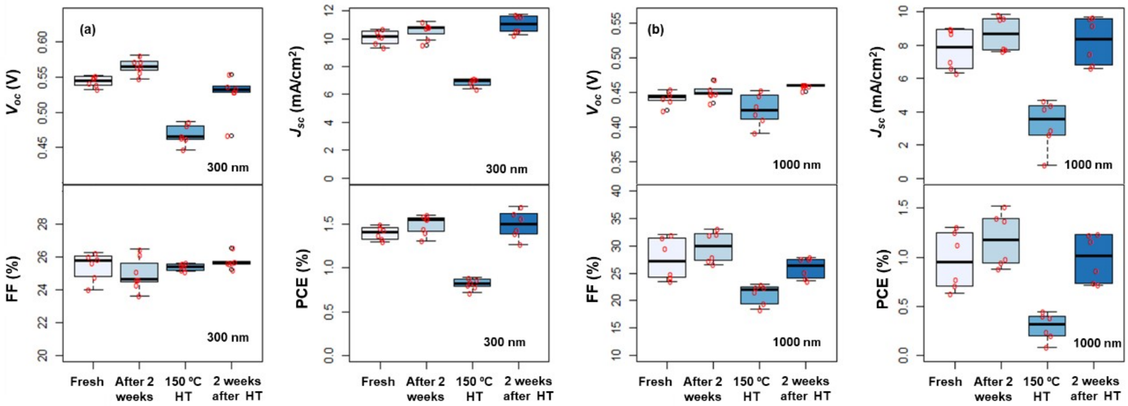

Figure S6. PV parameters extracted from the *J-V* curve under the illumination of the sequence were prepared to test the temperature stability. The samples were prepared with the x = 0.75 solutions, with an absorber thickness of a) 300 nm, and b) 1000 nm.

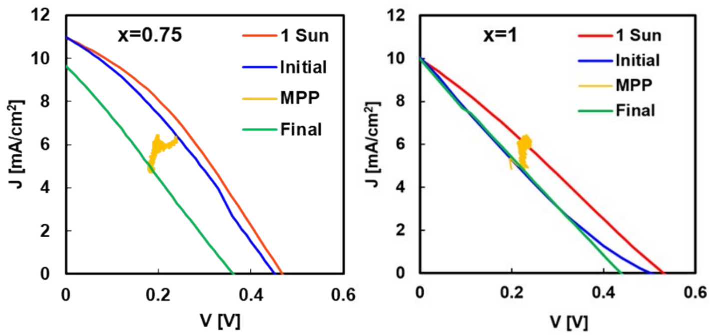

Figure S7. *J-V* curves of the samples, used for calibration of the halogen lamp under 1 Sun, under halogen illumination, and after the light stability test. The *J-V* points measured during the stability test are also marked. The slight variations between the curve at 1 Sun and the curve used for calibration, are associated with the different light spectrum, with a higher intensity of the infrared in the halogen lamp.

Supporting references:

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