

Supporting information

**Synergistic Effect of Mn on Bandgap Fluctuations and Surface
Electrical Characteristics in Ag-based $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Solar Cells**

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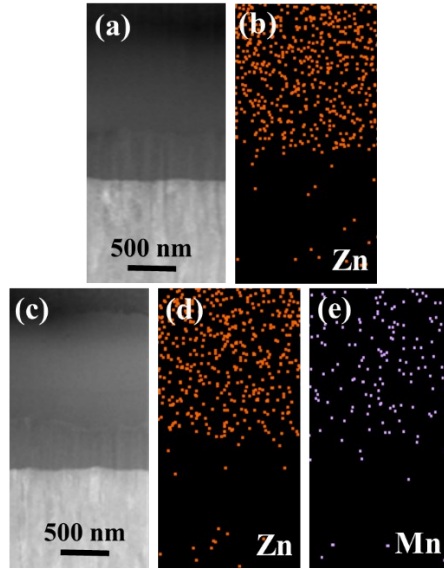


Fig. S1 TEM/EELS analysis of the CAZTSSe-based thin films. The high-angle annular dark field (HAADF) survey images of the S-Ref sample (a) and the S-10 sample (c). The qualitative elemental EELS maps of Zn and Mn elements for the S-Ref sample (b) and the S-10 sample (d, e), respectively.

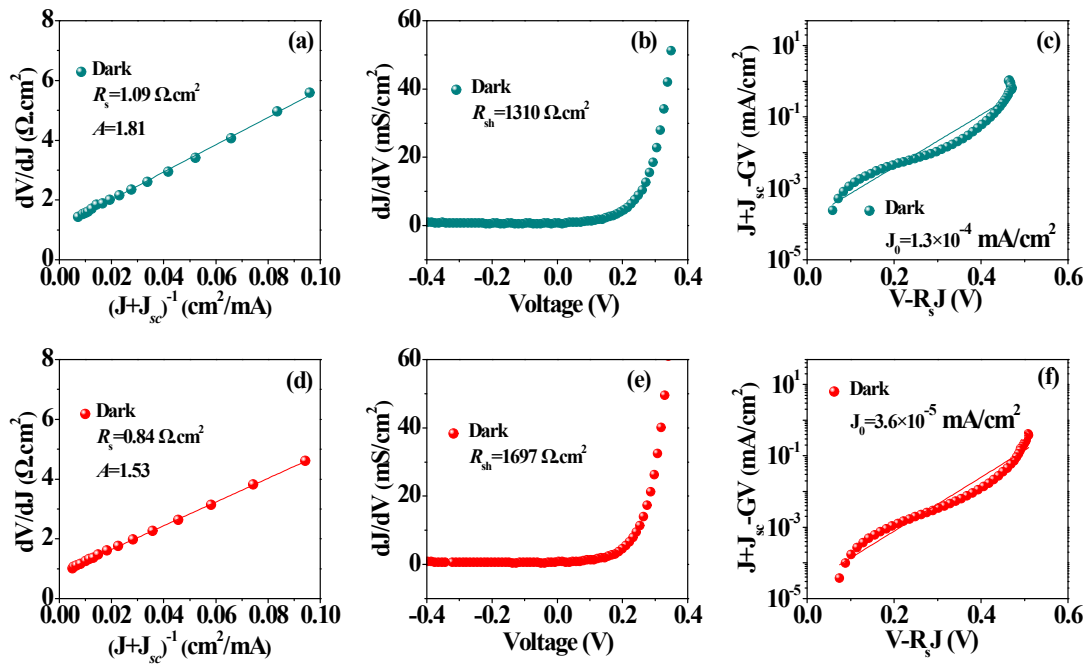


Fig. S2 Calculation of the diode parameters for the champion S-Ref and S-10 solar cells on the basis of dark J - V curves: (a-c) S-Ref sample and (d-f) S-10 sample. (a, d) series resistance R_s and diode quality factor A , (b, e) shunt resistance R_{sh} , (c, f) the reverse saturation current density J_0 .

Table S1. Summary of the photovoltaic parameters for $(\text{Cu}_{0.95}\text{Ag}_{0.05})_2(\text{Zn}_{1-x}\text{Mn}_x)\text{Sn}(\text{S},\text{Se})_4$ solar cells with different Mn content ($x=0.0-0.25$). The data are the average values calculated from 20 devices with standard deviation.

Sample	V_{oc} (mV)	J_{sc} (mA/cm ²)	Fill Factor (%)	Efficiency (%)
S-Ref	444.4±9.1	35.50±0.60	62.67±1.06	9.90±0.32
S-5	459.1±7.2	36.50±0.59	64.21±0.72	10.76±0.31
S-10	469.2±7.7	37.31±0.55	64.48±0.77	11.29±0.34
S-15	450.8±5.7	35.84±0.54	62.76±0.55	10.14±0.23
S-20	411.0±4.8	34.02±0.47	52.74±0.64	7.38±0.19
S-25	380.1±5.2	32.33±0.41	41.43±0.44	5.08±0.14

Table S2. The detailed ICP data of selenized S-Ref sample. The average values are calculated from 5 samples.

Sample	Cu	Ag	Zn	Sn	Se	(Cu+Ag)/ (Zn+Sn)	Zn/Sn
S1	0.95	0.048	0.681	0.547	1.991	0.813	1.245
S2	0.947	0.046	0.678	0.552	1.986	0.807	1.228
S3	0.948	0.051	0.675	0.55	2.015	0.816	1.227
S4	0.946	0.05	0.682	0.545	2.007	0.812	1.251
S5	0.952	0.049	0.679	0.544	2.004	0.818	1.248
Average	0.949	0.049	0.679	0.548	2.001	0.813	1.240

Table S3. The detailed ICP data of selenized S-10 sample. The average values are calculated from 5 samples.

Sample	Cu	Ag	Zn	Mn	Sn	Se	(Cu+Ag)/ (Zn+Mn+Sn)	(Zn+Mn)/ Sn	Mn/ (Mn+Zn)
S1	0.952	0.052	0.612	0.068	0.551	2.017	0.816	1.234	0.100
S2	0.948	0.05	0.61	0.067	0.545	1.995	0.817	1.242	0.099
S3	0.949	0.049	0.608	0.069	0.548	1.984	0.815	1.235	0.102
S4	0.947	0.051	0.613	0.068	0.549	2.011	0.811	1.240	0.100
S5	0.951	0.047	0.607	0.068	0.543	2.006	0.819	1.243	0.101
Average	0.949	0.050	0.610	0.068	0.547	2.003	0.816	1.239	0.100

Table S4. The detailed lattice constants of S-Ref sample. The average values are calculated from 5 samples with standard deviation.

Sample	S1	S2	S3	S4	S5	Average	
Lattice constant calculated	a (Å)	5.671	5.673	5.662	5.657	5.670	5.667±0.007
	c (Å)	11.319	11.320	11.310	11.323	11.315	11.317±0.005

Table S5. The detailed lattice constants of S-10 sample. The average values are calculated from 5 samples with standard deviation.

Sample		S1	S2	S3	S4	S5	Average
Lattice constant	a (Å)	5.686	5.681	5.692	5.695	5.683	5.687±0.006
calculated	c (Å)	11.326	11.323	11.329	11.333	11.327	11.328±0.004