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Supporting Information

Mapping the Energetics of Defect States in $\text{Cu}_2\text{ZnSnS}_4$ films and the Impact of Sb Doping

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Figure S1 and **S2** present the representative J-V characteristics under AM1.5 illumination and the spectral response of external quantum efficiency (EQE), contrasting the solar cell performance of devices incorporating no-dopants, Sb-doped and Na:Sb codoped CZTS films. The J-V curves clearly show a marked change in the V_{oc} and FF . Inset to **Figure S1** is a table of the performance parameters of solar cells. Similarly, EQE spectra (**Figure S2**) show a better charge collection at the longer wavelengths and a sharper CZTS absorption edge, indicating a lowering of the disorder in CZTS upon doping. Using the wavelength derivative of EQE in the neighbourhood of CZTS absorption, we calculate the bandgaps of the three CZTS layers (no-dopants and doped) to all be close to 1.4 eV (**Figure S3**) and to match the values obtained from diffuse reflectance spectroscopy in previous work.¹ As mentioned in the introduction, the kesterites suffer from a variety of forms of disorder which often result in tailing of the band edges.

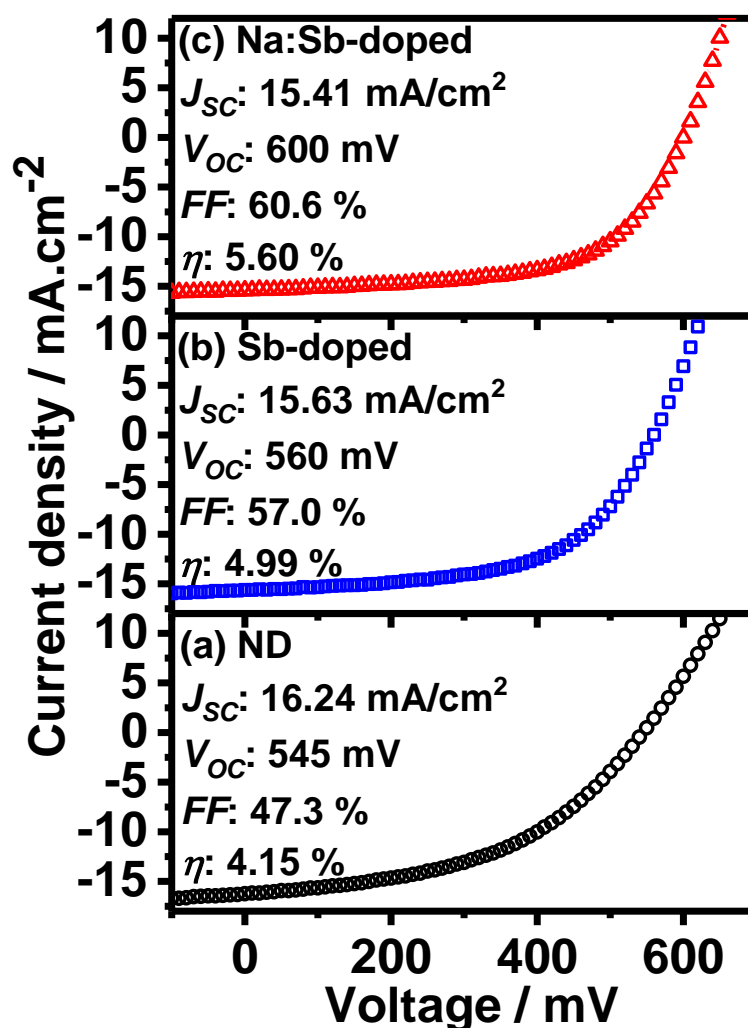


Figure S1: J-V Characteristics of ND (a), Sb-doped (b) and Na:Sb-doped (c) CZTS solar cells under simulated AM 1.5G (100 mW/cm²) illumination along with the performance metrics of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill-factor (FF) and efficiency (η).

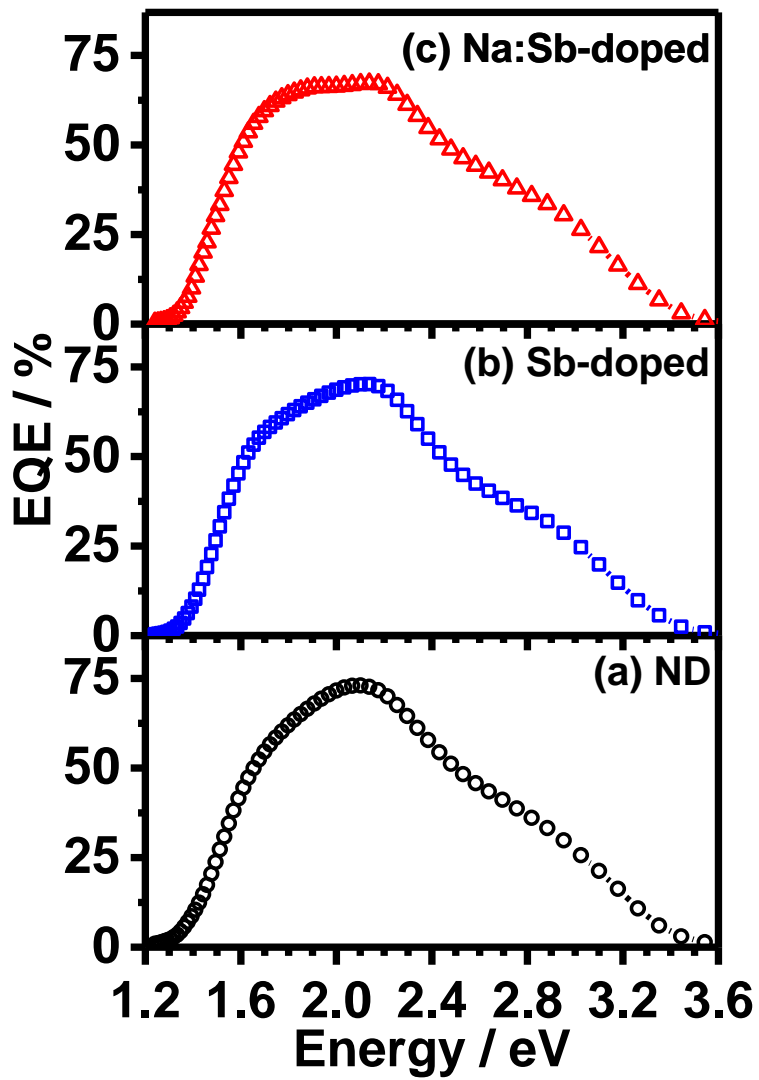


Figure S2: Spectral response of external quantum efficiency (EQE) of ND (a), Sb-doped (b) and Na:Sb-doped (c) CZTS solar cells.

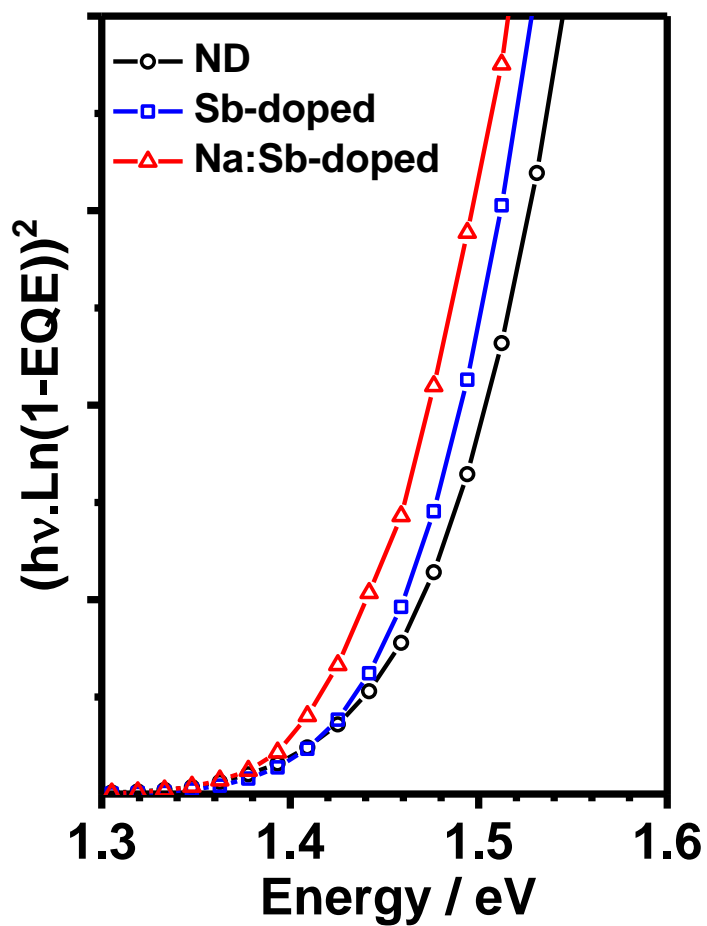


Figure S3: Tauc-like plot to estimate the bandgap of CZTS from EQE data

Table S1: Statistical analysis of the performance metrics of solar cells based on ND, Sb-doped, Na:Sb-codoped CZTS. In total 216 devices were analysed including 72 devices for each type of sample.

Average values of performance metrics \pm standard deviation (Best value)				
	V_{oc} / mV	J_{sc} / mA.cm ⁻²	FF / %	Efficiency / %
ND	492.09 \pm 46.32 (550.29)	12.94 \pm 2.03 (16.26)	42.77 \pm 2.62 (47.10)	3.21 \pm 0.64 (4.21)
Sb-doped	526.46 \pm 43.54 (563.08)	15.03 \pm 0.74 (15.25)	50.36 \pm 3.14 (58.84)	4.70 \pm 0.29 (5.05)
Na:Sb-doped	548.85 \pm 27.55 (609.87)	15.48 \pm 0.85 (14.89)	53.16 \pm 2.55 (62.98)	5.04 \pm 0.35 (5.72)

Table S2: Summary of various defect states and optoelectronic parameters measured from EQE, admittance and PL spectroscopies. All the numbers are in the units of eV.

Method	Parameter	Assignment	ND	Sb-doped	Na:Sb-doped
Assumed	VBM	VBM (eV)	0	0	0
EQE	CBM	CBM (eV)	1.41	1.41	1.41
Admittance	$E_{A,CfT}^1$		0.035	0.062	0.028
Admittance	$E_{A,CfT}^2$	$E_A - E_V$ (eV)	0.106	0.236	0.125
Admittance	$E_{A,CfT}^3$		0.359	-	-
PL	W_1 or $E_{A,PL}^{1,Sb}$	Γ (eV)	0.035	0.018	0.022
PL	$E_{A,PL}^2$	$E_C - E_D$ (eV)	0.121	0.077	0.126
PL	E_{Peak}	Peak position (eV)	1.15	1.06	1.17
PL	$E_{Peak} + (E_A + E_D) + 2\Gamma$	QDAP (eV)	1.45	1.41	1.43
Admittance					
EQE, diffuse reflectance	Band gap	E_g (eV)	1.41	1.41	1.41

Reference

- (1) Tiwari, D.; Koehler, T.; Lin, X.; Harniman, R.; Griffiths, I.; Wang, L.; Cherns, D.; Klenk, R.; Fermin, D. J. Cu₂ZnSnS₄ Thin-Films Generated from a Single Solution Based Precursor: The Effect of Na and Sb Doping. *Chem. Mater.* **2016**, *28*, 4991–4997.