materials

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Supplementary Material

Fabrication of Cu_2ZnSnS_4 Light Absorber Using a Cost-Effective Mechanochemical Method for Photovoltaic Applications

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Characterization

The prepared CZTS thin films were analyzed using various characterization techniques, such as X-ray diffraction (XRD), Raman spectroscopy, field-emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDS), Fourier-transform infrared (FT-IR) spectroscopy, ultraviolet-visible near-infrared (UV-Vis-NIR) spectroscopy, and Hall measurements. The crystallographic information of the as-fabricated and annealed thin films was evaluated using an X-ray diffractometer (PANalytical X′ Pert-PRO MPD) with monochromatized Cu Kα radiation (λ = 1.5406 Å). The XRD patterns were recorded in the 2θ range of 10°–80° at a 4°/min scanning rate and a step size of 0.02°. Phase analysis of the CZTS samples was carried out using a Jobin-Yvon-Horiba (model no-HR800UV) Raman spectrometer at room temperature with a 514.5 nm laser and a working power of 10 mW. The surface morphology and cross-sectional structure of the samples were observed using FE-SEM (Hitachi, model no-S-4800). EDS was used to study the chemical composition of the samples. The optical properties of all CZTS thin films were measured in the wavelength range of 300–2500 nm using a UV-Vis-NIR spectrometer (Varian, model no-UV-5000). The electrical properties were investigated using the Hall effect measurement (model no-HMS5000) with the Van der Pauw approach with the current in the range of 1.0–0.1 nA and magnetic field intensity of 0.55 T at room temperature. Ag paste was used to make a metal contact at the corner of the thin film. FT-IR spectra were collected using a PerkinElmer FT-IR spectrometer (model no., Spectrum-100) in the KBr mode. The current density-voltage (J–V) curve of the 0.4 x 0.4 cm^2 fabricated solar cells was measured with a Keithley (model no., 2400). A Xe flash lamp (USHIO, flash type, UA-DF1, 1,000 W, 400 V) with a standard AM1.5 (100 mW cm^{-2}) filter was used as the light source.

Figure S1:

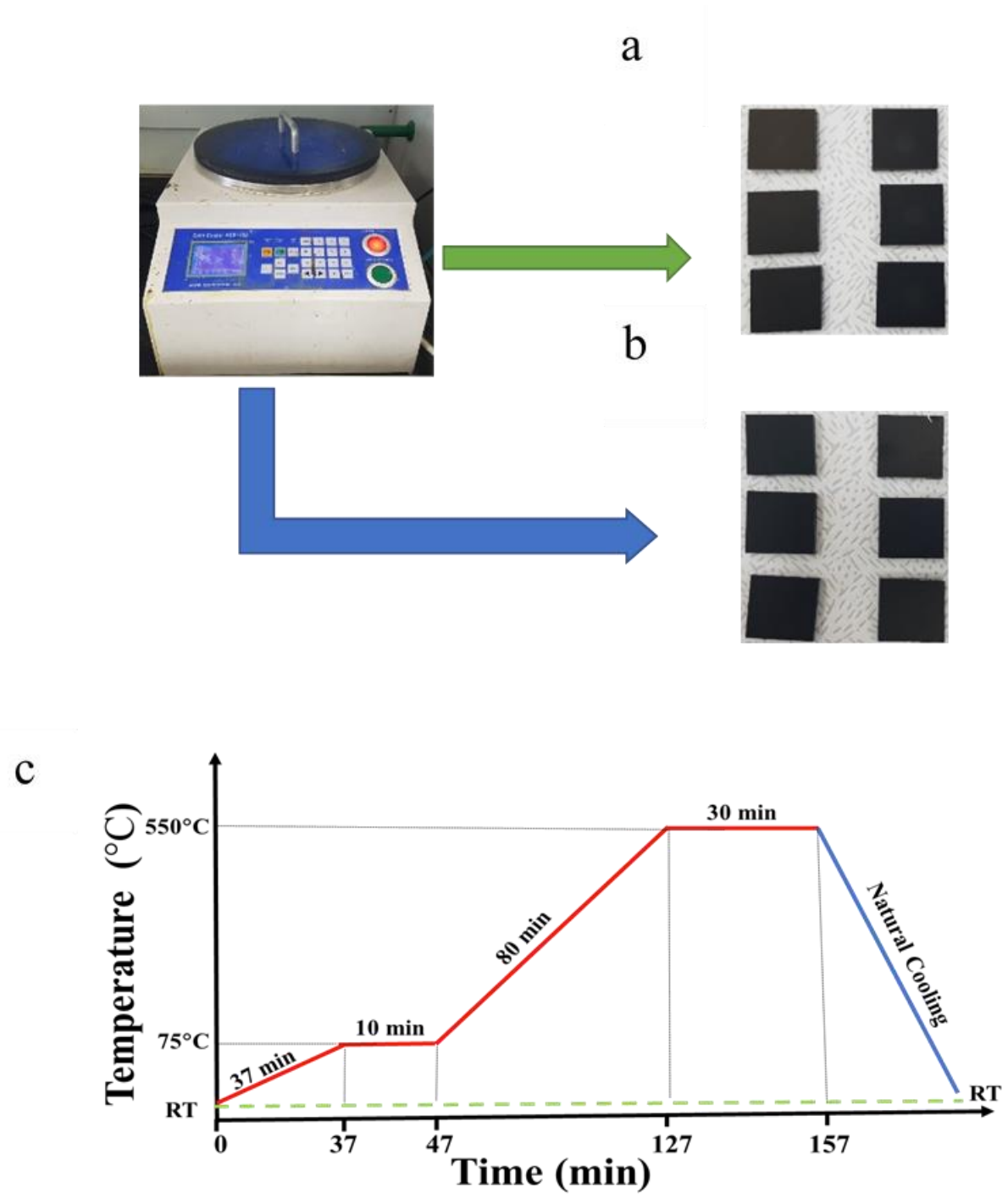

Figure S1. Spin Coating process for deposition of Cu_2ZnSnS_4 thin films (a) without and (b) with a sodium solution, (c) Annealing profile of Cu_2ZnSnS_4 thin films.

Figure S2:

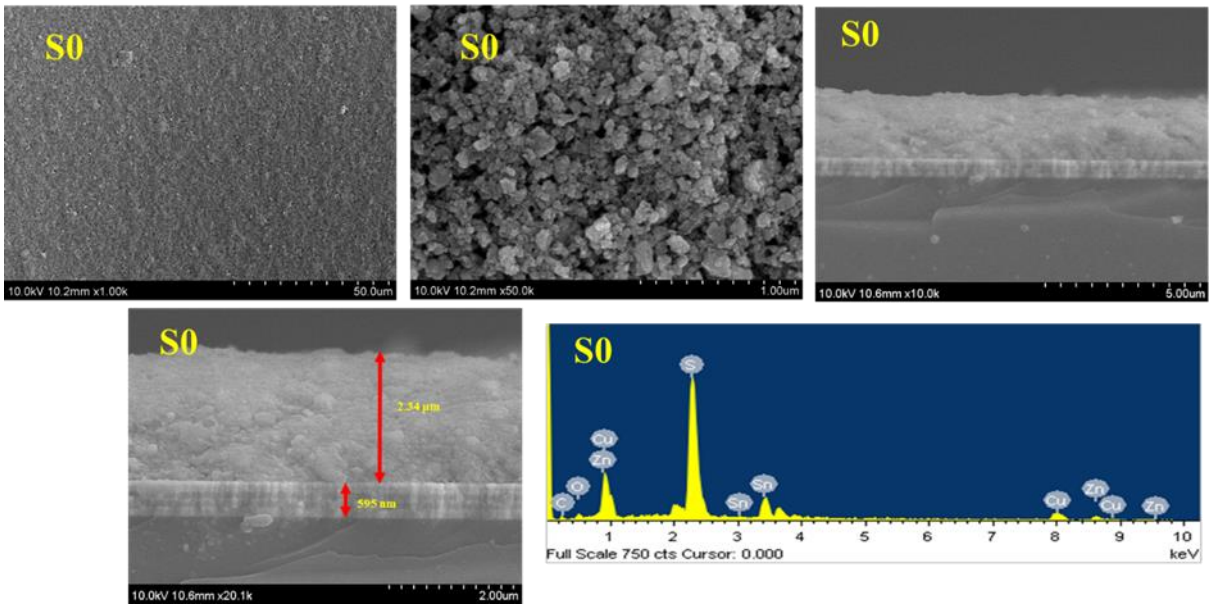

Figure S2. Surface and cross-section images and EDX spectrum of S0 thin film.

Figure S3:

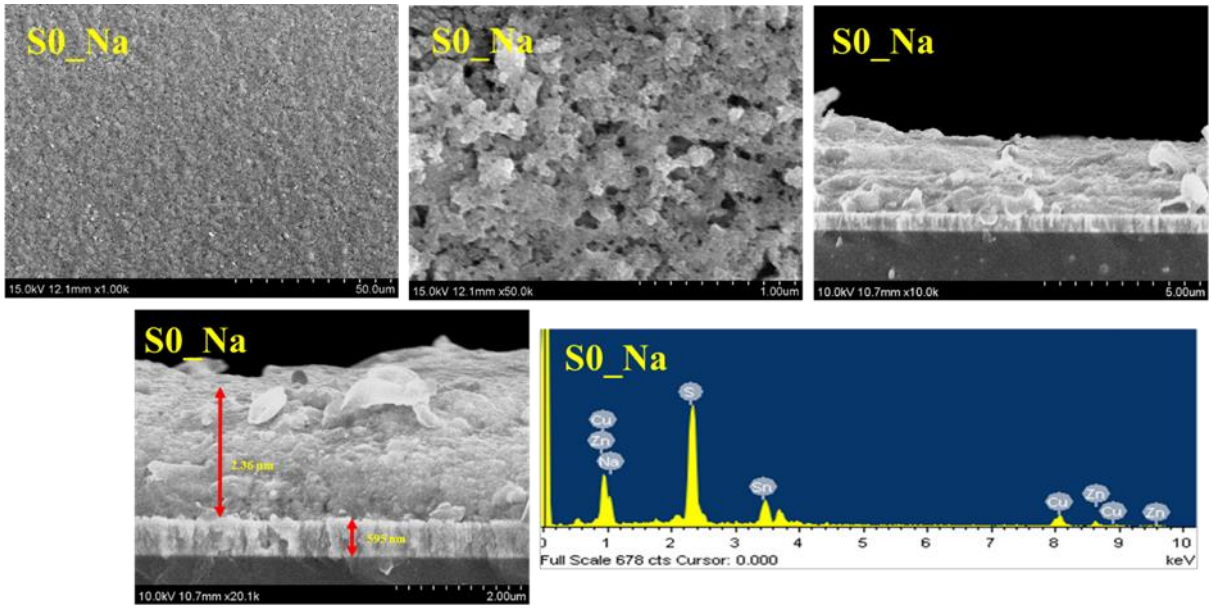

Figure S3. Surface and cross-section images and EDX spectrum of S0_Na thin film with sodium layer.

Figure S4:

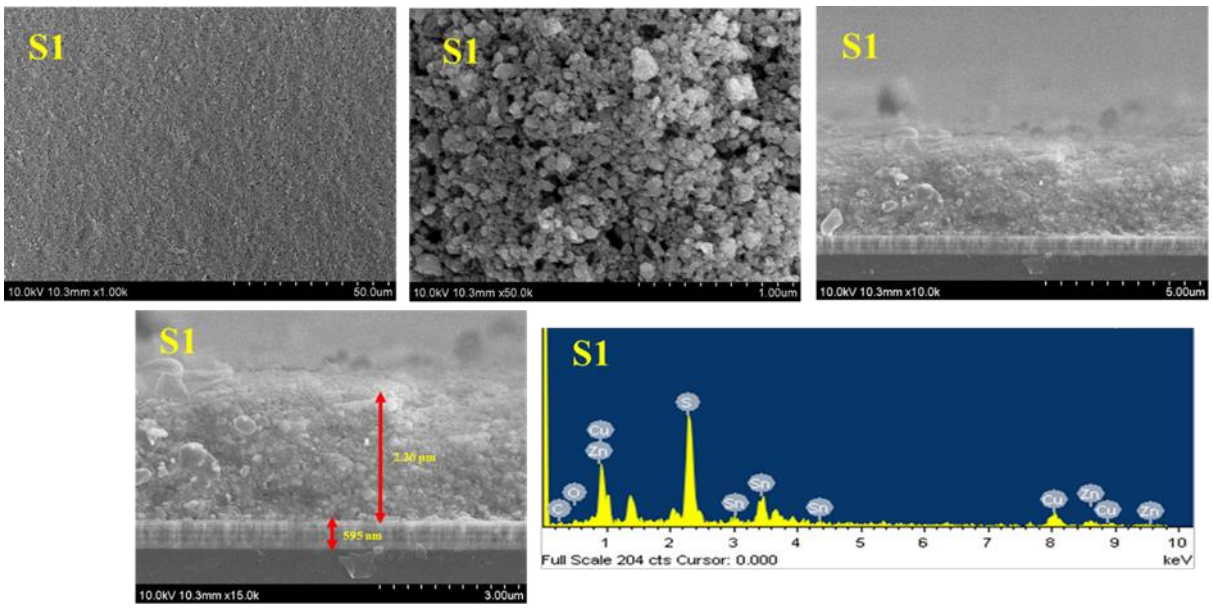

Figure S4. Surface and cross-section images and EDX spectrum of S1 thin film.

Figure S5:

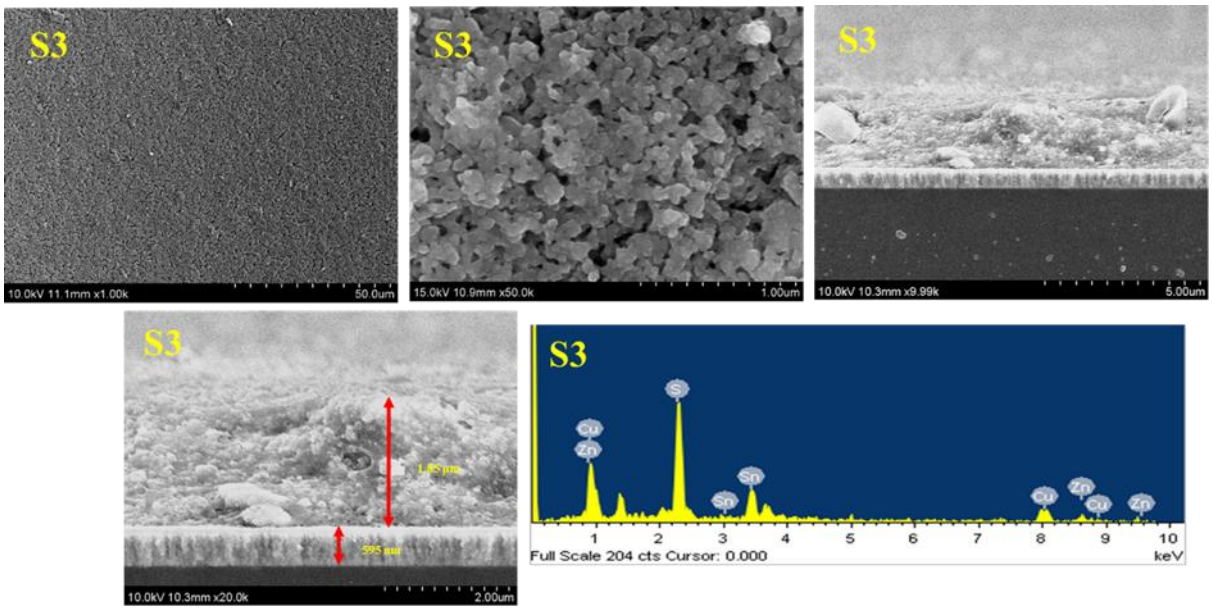

Figure S5. Surface and cross-section images and EDS spectra of S3 thin film with sodium layer

Figure S6:

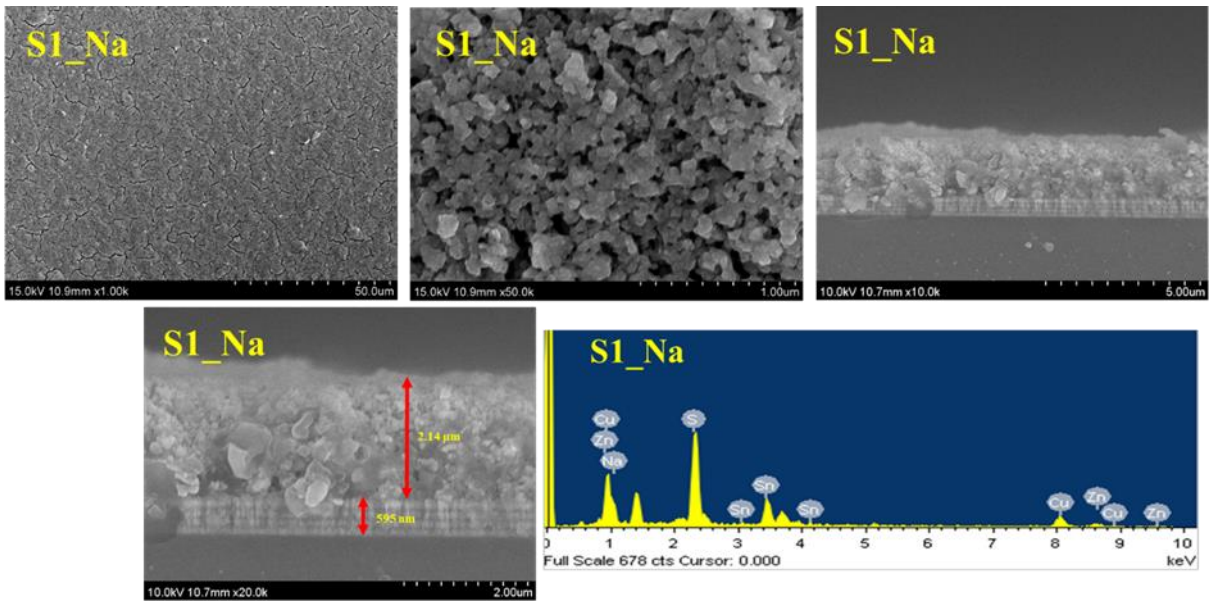

Figure S6. Surface and cross-section images and EDS spectra of S1_Na thin film.

Figure S7:

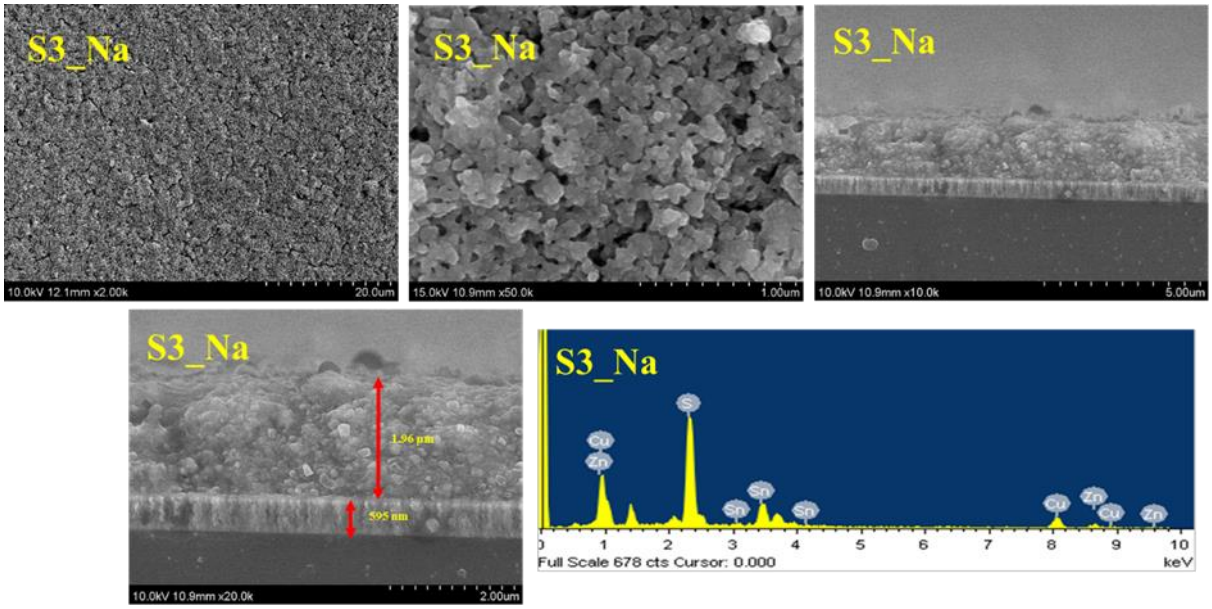

Figure S7. Surface and cross-section images and EDS spectra of S3_Na thin film with sodium layer.

Table S1. Raman scattering band position of Cu_2ZnSnS_4 and other secondary phases.

Sl. No.	Phase	Raman peak position	Ref.
1	**Cu_2ZnSnS_4**	**289, 338, 358, 370**	[S1] [S2] [S3] [S4]
2	**Hexa-ZnS**	**355**	[S5]
3	**Cubic ZnS**	**348**	[S2]
4	**$Cu_2Sn_3S_7$**	**268, 318, 375**	[S6]
5	**Ort.Cu_3SnS_4**	**318**	[S2]
6	**Monoclinic Cu_2SnS_3**	**290, 352**	[S7]
7	**Tetrg.Cu_2SnS_3**	**297, 337, 352**	[S2],[S7]
8	**Cubic Cu_2SnS_3**	**267, 303, 356**	[S2],[S7]
9	**$Cu_{2-x}S$**	**475**	[S8]
10	**Sn_2S_3**	**32,60,307**	[S9]
11	**SnS_2**	**315**	[S10]
12	**SnS**	**96, 163, 189, 220, 288**	[S10]

Table S2. Elemental composition of Cu_2ZnSnS_4 without and with sodium layer.

Sl No	Sample Name	Cu%	Zn%	Sn%	S%	Na%	C%	O%
1	**S0**	**15.70**	**7.90**	**6.83**	**39.11**	**-**	**19.37**	**11.37**
2	**S1**	**26.97**	**16.28**	**11.52**	**45.23**	**-**	**-**	**-**
3	**S2**	**26.99**	**15.34**	**12.78**	**44.89**	**-**	**-**	**-**
4	**S3**	**26.38**	**12.87**	**12.73**	**48.02**	**-**	**-**	**-**
5	**S0_Na**	**13.83**	**5.83**	**5.61**	**38.62**	**3.70**	**17.45**	**14.96**
6	**S1_Na**	**26.35**	**12.68**	**12.09**	**43.42**	**5.45**	**-**	**-**
7	**S2_Na**	**24.26**	**11.52**	**12.04**	**45.51**	**6.68**	**-**	**-**
8	**S3_Na**	**24.60**	**10.78**	**10.93**	**48.52**	**5.16**	**-**	**-**

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