

Supporting Information

The Deposition of $\text{Cu}_2(\text{Zn}_y\text{Fe}_{1-y})\text{SnS}_4$, $\text{Cu}_2(\text{Zn}_y\text{Fe}_{1-y})\text{SnSe}_4$ and $\text{Cu}_2(\text{Zn}_y\text{Fe}_{1-y})\text{Sn}(\text{S}_x\text{Se}_{1-x})_4$ Thin Films by AACVD

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X-ray Diffraction Studies

Rietveld refinements of p-XRD patterns

Table S1: Rietveld analysis results of CZFTS thin films deposited at 350°C using the molar ratio 2:1:0.5:0.5:1 of $[\text{Cu}(\text{S}_2\text{CNET}_2)_2]:[\text{Fe}(\text{S}_2\text{CNET}_2)_3]:[\text{Zn}(\text{S}_2\text{CNET}_2)_2]:[\text{nBu}_2\text{Sn}(\text{S}_2\text{CNET}_2)_2]$ precursors in 20 ml THF. Fitted against Zn- rich $\text{Cu}_2\text{Fe}_{0.3}\text{Zn}_{0.7}\text{Sn}_1\text{S}_4$ phase (ICDD 04-015-0225) with resultant lattice parameters $a = 5.41$ (2) Å and $c = 10.86$ (4) Å. $R_{wp} = 2.85$.

	h	k	l	m	d	2θ
1	1	1	0	4	3.82760	23.21996
2	1	1	2	8	3.12848	28.50799
3	0	1	3	8	3.00914	29.66405
4	0	0	4	2	2.71503	32.96427
5	0	2	0	4	2.70652	33.07088
6	0	2	2	8	2.42230	37.08435
7	2	1	1	16	2.36280	38.05370
8	1	1	4	8	2.21449	40.71109
9	0	1	5	8	2.01580	44.93145
10	2	1	3	16	2.01231	45.01365
11	2	0	4	8	1.91680	47.38986
12	2	2	0	4	1.91380	47.46874
13	0	0	6	2	1.81002	50.37407
14	2	2	2	8	1.80497	50.52475
15	0	3	1	8	1.77995	51.28628
16	3	1	0	8	1.71175	53.48805
17	1	1	6	8	1.63629	56.16724
18	3	1	2	16	1.63256	56.30699
19	2	1	5	16	1.61667	56.91050
20	0	3	3	8	1.61487	56.97981
21	2	2	4	8	1.56424	59.00238
22	0	2	6	8	1.50457	61.59058
23	0	1	7	8	1.49140	62.19477
24	3	2	1	16	1.48716	62.39162
25	3	1	4	16	1.44799	64.27829
26	0	3	5	8	1.38792	67.42177
27	3	2	3	16	1.38678	67.48466
28	0	0	8	2	1.35751	69.14278
29	0	4	0	4	1.35326	69.39124
30	2	2	6	8	1.31504	71.71373
31	0	4	2	8	1.31310	71.83605
32	2	1	7	16	1.30621	72.27411
33	4	1	1	16	1.30337	72.45698
34	1	1	8	8	1.27943	74.03570
35	3	3	0	4	1.27587	74.27724
36	3	1	6	16	1.24368	76.54020
37	3	3	2	8	1.24204	76.65964

38	3	2	5	16	1.23500	77.17695
39	4	1	3	16	1.23420	77.23652
40	0	2	8	8	1.21343	78.81156
41	0	4	4	8	1.21115	78.98916
42	4	2	0	8	1.21039	79.04833
43	4	2	2	16	1.18140	81.38853
44	0	1	9	8	1.17777	81.69240
45	0	3	7	8	1.17638	81.80980

Table S2: Rietveld analysis results of CZFTS thin films deposited at 350°C using the molar ratio 2 : 1 : 0.7 : 0.3 : 1 of [Cu(S₂CNET₂)₂] : [Fe(S₂CNET₂)₃] : [Zn(S₂CNET₂)₂] : [nBu₂Sn(S₂CNET₂)₂] precursors in 20 ml THF. Fitted against Fe – rich phase of Cu₂Fe_{0.7}Zn_{0.3}Sn₁S₄ (ICDD: 01-015-0228) with resultant lattice parameters a = 5.42Å, c = 10.83Å and Rwp = 2.43.

	h	k	l	m	d	th2
1	1	1	2	8	3.12702	28.52165
2	0	1	3	8	3.00404	29.71556
3	0	2	0	4	2.70833	33.04818
4	0	0	4	2	2.70757	33.05762
5	0	2	2	8	2.42227	37.08490
6	2	1	1	16	2.36399	38.03374
7	1	1	4	8	2.21093	40.77952
8	2	1	3	16	2.01152	45.03220
9	0	1	5	8	2.01121	45.03948
10	2	2	0	4	1.91508	47.43512
11	0	2	4	8	1.91481	47.44212
12	2	2	2	8	1.80550	50.50914
13	0	0	6	2	1.80505	50.52248
14	0	3	1	8	1.78097	51.25464
15	3	1	0	8	1.71290	53.44952
16	3	1	2	16	1.63314	56.28506
17	1	1	6	8	1.63281	56.29744
18	0	3	3	8	1.61484	56.98070
19	2	1	5	16	1.61468	56.98684
20	2	2	4	8	1.56351	59.03282
21	0	2	6	8	1.50202	61.70654
22	3	2	1	16	1.48806	62.34978
23	0	1	7	8	1.48769	62.36722
24	3	1	4	16	1.44755	64.30038
25	3	2	3	16	1.38701	67.47207
26	0	3	5	8	1.38690	67.47764
27	0	4	0	4	1.35416	69.33832
28	0	0	8	2	1.35379	69.36033
29	0	4	2	8	1.31371	71.79729
30	2	2	6	8	1.31354	71.80814
31	4	1	1	16	1.30417	72.40511
32	2	1	7	16	1.30392	72.42131
33	3	3	0	4	1.27672	74.21935
34	1	1	8	8	1.27640	74.24075
35	3	3	2	8	1.24265	76.61543
36	3	1	6	16	1.24250	76.62601
37	4	1	3	16	1.23453	77.21189
38	3	2	5	16	1.23446	77.21717
39	4	2	0	8	1.21120	78.98526
40	0	4	4	8	1.21113	78.99051
41	0	2	8	8	1.21093	79.00624
42	4	2	2	16	1.18199	81.33876
43	0	3	7	8	1.17485	81.93898
44	0	1	9	8	1.17473	81.94939

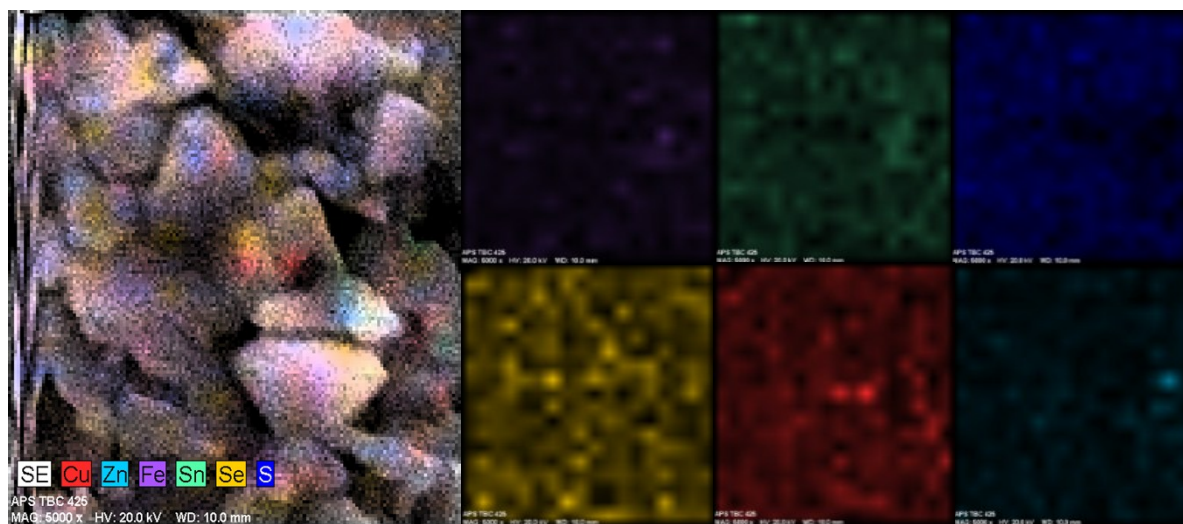


Figure S1: Elemental map of CZFTSSe thin film obtained at 350 °C.

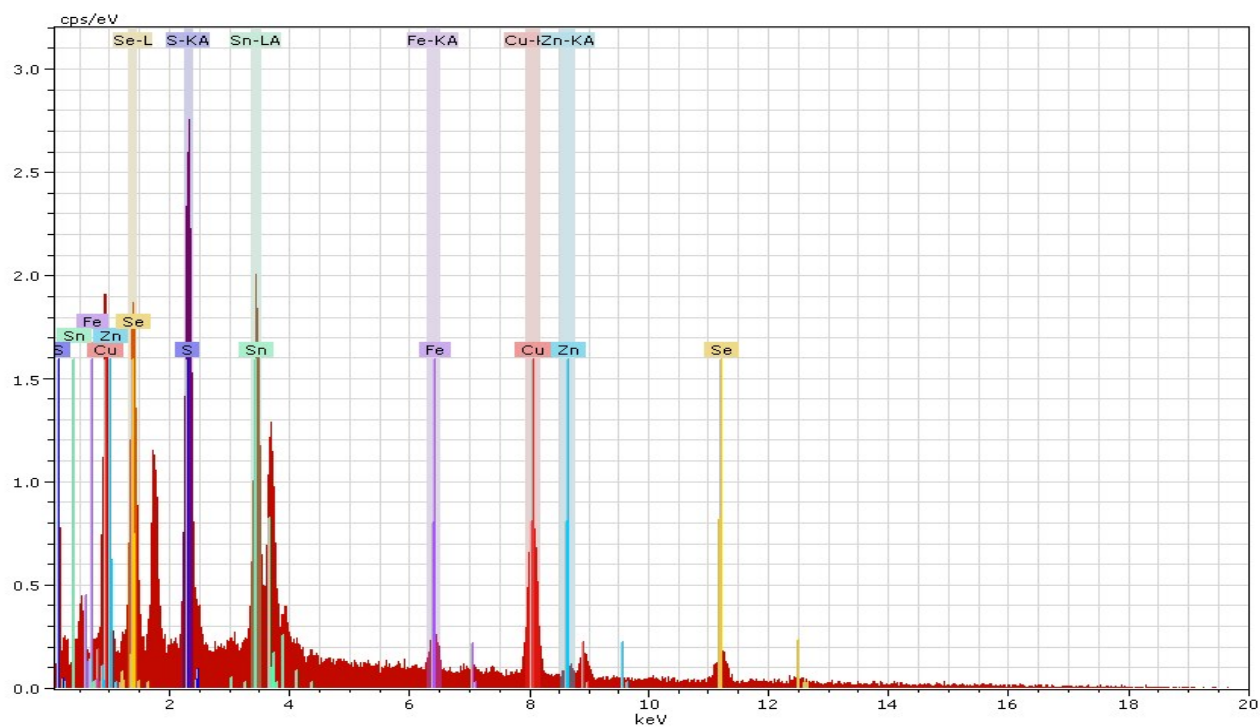
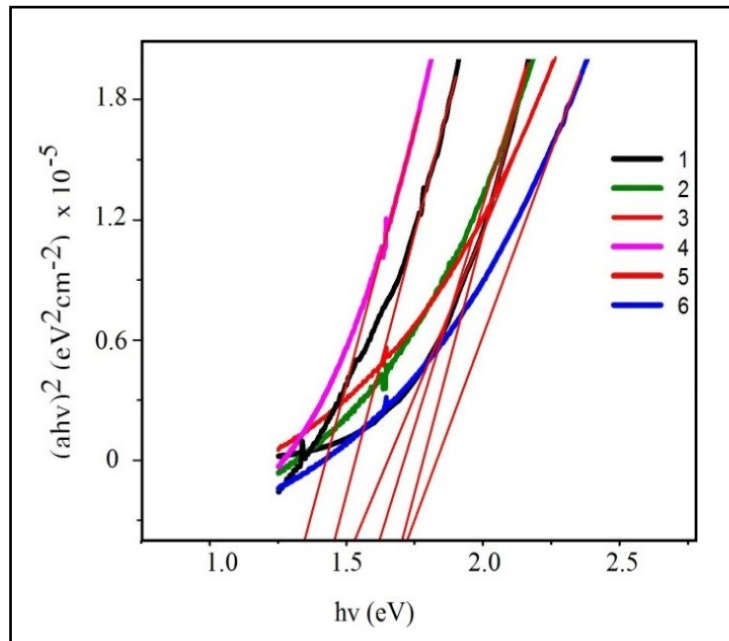


Figure S2: Elemental map/ EDX result of CZFTSSe thin film obtained at 350 °C.

Table S3: Band gap measurement from Tauc Plots.

Material	% Fe (y)	Intercept (a)	Slope (b)	BG (eV)	R ²
$\text{Cu}_2(\text{Zn}_y\text{Fe}_{1-y})\text{SnSe}_4$	3	2.66E-04	1.80E-04	1.48	8.994
$\text{Cu}_2(\text{Zn}_y\text{Fe}_{1-y})\text{SnSe}_4$	7	4.25E-05	2.89E-05	1.47	7.885
$\text{Cu}_2(\text{Zn}_y\text{Fe}_{1-y})\text{Sn}(\text{S}_x\text{Se}_{1-x})_4$	4	4.79E-05	2.98E-05	1.61	9.192
$\text{Cu}_2(\text{Zn}_y\text{Fe}_{1-y})\text{Sn}(\text{S}_x\text{Se}_{1-x})_4$	6	7.17E-05	4.37E-05	1.64	9.822
$\text{Cu}_2(\text{Zn}_y\text{Fe}_{1-y})\text{SnS}_4$	3	2.49E-04	1.49E-04	1.67	8.792
$\text{Cu}_2(\text{Zn}_y\text{Fe}_{1-y})\text{SnS}_4$	7	7.60E-04	4.42E-04	1.72	9.324

**Figure S3:** UV- Vis Tauc plots of CZFTSe (1,2), CZFTSSe (3, 4) and CZFTS (5, 6), thin films deposited at 350 °C using different Zn and Fe precursor composition, y represent mole fraction of Zn.

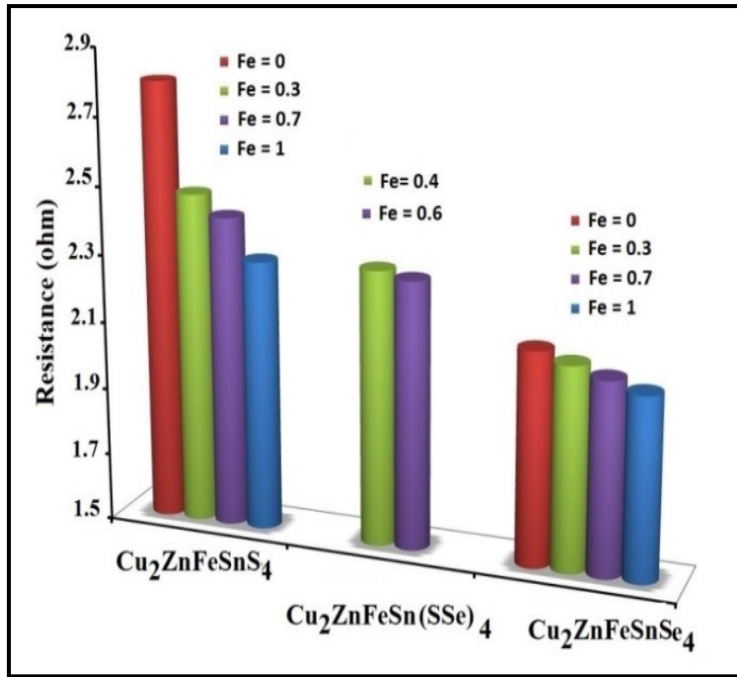


Figure S4 : Variation of electrical resistance with stoichiometric ratio of Fe for CZFTS, CZFTSe and CZFTSSe thin films deposited at 350 °C.

