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The AACVD of $Cu_2FeSn(S_xSe_{1-x})_4$: A Family of Environmentally Benign Solar Cells Materials

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Synthesis of Precursors

Complexes $[Cu(S_2CNEt_2)_2]$,[1] (**1**) $[Fe(S_2CNEt_2)_3]$[2] (**2**) and $[Bu_2Sn(S_2CNEt_2)_2]$[3] (**3**) were synthesised using the methods reported previously. Thermal decomposition studies were done by thermogravimetric analysis (TGA) and the results were matching with the reported values (Figure S1).All complexes decompose at same range of temperature.

Synthesis of $[Cu(S_2CNEt_2)_2]$ (**1**) **:** Sodium salt of diethyldithiocarbamate (3 g, 1.3 mmol) was dissoloved in 50 mL of methanol in double neck 250 mL RB. Slow addition of methanolic solution of $Cu(NO_3)2$ (1.24 g, 0.65 mmol) gave black precipitate. Precipitate formed was isolated by filtration. Recrystallisation was performed using chloroform. Yield: 4.78g (73%), Mpt: 201 °C, IR (vmax/cm-1): 2979(w), 2868(w), 1501(s), 1434(m), 1270(s), 1205(m) and 1144(m), Elemental analysis: Calc. for $C_{10}H_{20}N_2S_4Cu$: C, 33.4; H, 5.5; N, 7.7; S, 35.6; Cu, 17.6 %. Found: C, 33.2; H, 5.3; N, 7.3; S, 35.2; Cu, 17.2 %.

Synthesis of $[Fe(S_2CNEt_2)_3]$ (**2**) : This complex was synthesised by method described for complex (1) using zinc acetate (1.46 g, 0.65 mmol), The crude product was obtained as white powder. Recrystallisation from chloroform, yielded colourless crystals. yield 4.81 g (79%), Mpt: 198-201 °C, IR (vmax/cm-1): 2967(w), 2938(w), 1478(s), 1429(m), 1352(w), 1296(w), 1296(m), 1270(s), 1050(s) and 950(s), Elemental analysis: Calc. for $C_{15}H_{30}N_3S_6Fe$: C, 35.98; H, 6.04 N, 8.39; S, 38.43; Fe, 11.15 %. Found: C, 35.7; H, 6.3; N, 8.4; S, 37.82; Fe, 11.0 %.

Synthesis of $[Bu_2Sn(S_2CNEt_2)_2]$ (**3**): Complex 3 was synthesised by method described for complex (1) using di-n-butyltin dichloride (2.02 g. 0.65 mmol). The methanol was removed by vacuum distillation. Recrystallization using ethanol-chloroform yielded colourless plates of crystals. White solid, yield 5.5 g, (67%), Mpt: 57 °C, IR (vmax/cm-1): 2953(w), 2924(w), 1483(s), 1456(m), 1417(s), 1353(m), 1298(m) 1253(s), 1205(s) and 1138(s), Elemental analysis: Calc. for $C_{18}H_{38}N_2S_4Sn$: C, 40.8; H, 7.2; N, 5.3; S, 24.2; Sn, 22.4 %. Found: C, 39.9; H, 7.5; N, 5.1; S, 22.8; Sn, 21.4 %.were synthesised using the method reported previously.

Synthesis of $Cu(PPh_3)[Ph_2P(Se)NP(Se)Ph_2]$(**4**): Step one involved the synthesis of potassium diphenylphosphinodiselenoate by reaction of diphenylphosphine, elemental selenium and potassium hydroxide as reported by Gusarova et al.[4] In step a 150 mL methanol solution of 1.2 g (2.6 mmol) $K[Ph_2P(Se)P(Se)Ph_2]$ was mixed with a solution of $Cu(PPh_3)_2NO_3$ (1.4 g, 2,1 mmol) in 100 mL chloroform. Stirred for 30 min and the precipitate was filtered , filtrate on rotary evaporation gave a pinkish powder. The product was recrystallized from CH_2Cl_2. Yield: 64% $Cu(PPh_3)[Ph_2P(Se)NP(Se)Ph_2]$; m. p; 221-223 °C. Elemental Analysis : Calc. for $C_{42}H_{35}CuNP_3Se_2$: C, 58.1; H, 4.1; N, 1.6% and Found C, 57.87; H, 3.92; N, 1.48. 31P NMR (400 MHz, $CDCl_3$, rel. to

85% H_3PO_4): δ = 26.14 ppm with two P–Se satelites, 1JP–Se-576 Hz. FTIR: 3050 cm^{-1}(n C- H), 1165 cm^{-1} (n -P2N),1100, 755 cm^{-1} (ns-P2N), 690, 545 (n- PSe), 519, 505. Mass spec: m/z : 869 ,670, 460, 341. TGA showed single step decomposition between 250 to 320 °C with residue ~ 15% which is closer to the expected CuSe (16%) (Figure S1)

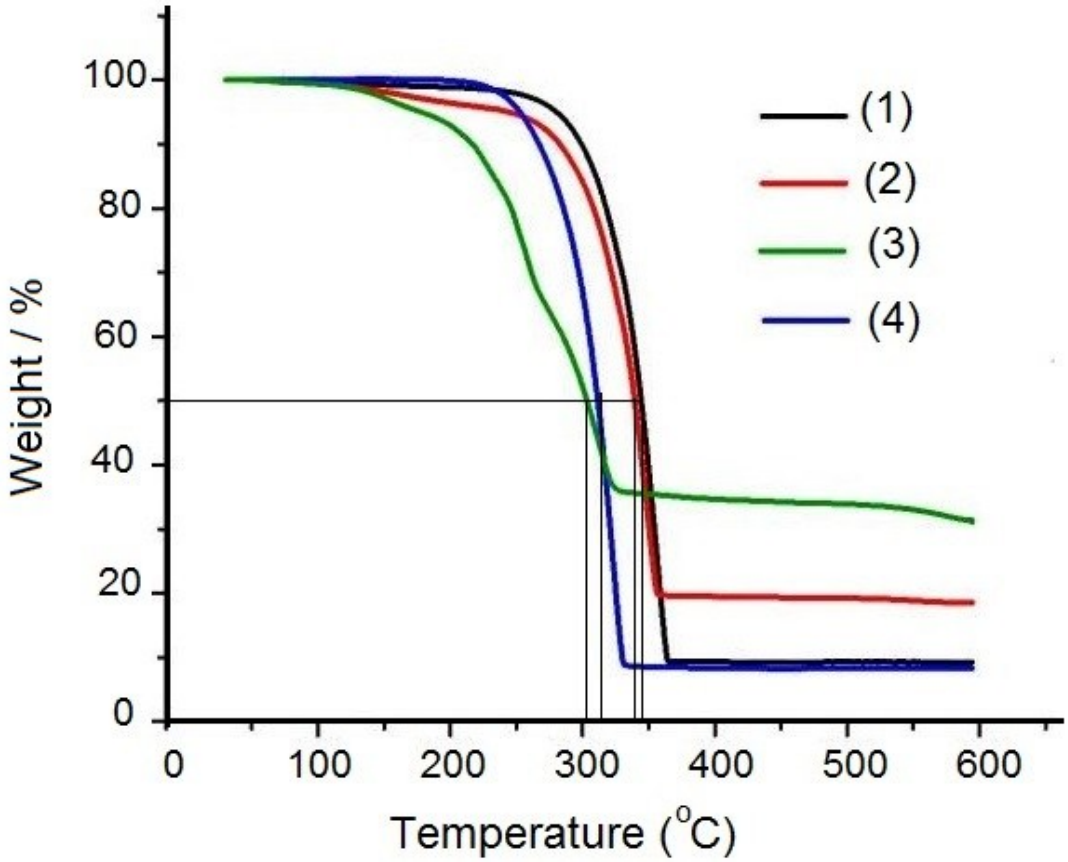

Figure S1: TGA analysis of precursors (**1-4**). Black vertical lines represent 50 % decomposition temperatures 349, 345,302 and 310 °C for precurosros (1) to (4) respectively. Thermal decomposition studies were carried from 10-600 °C, at a heating rate 10 °C min^{-1} under nitrogen.

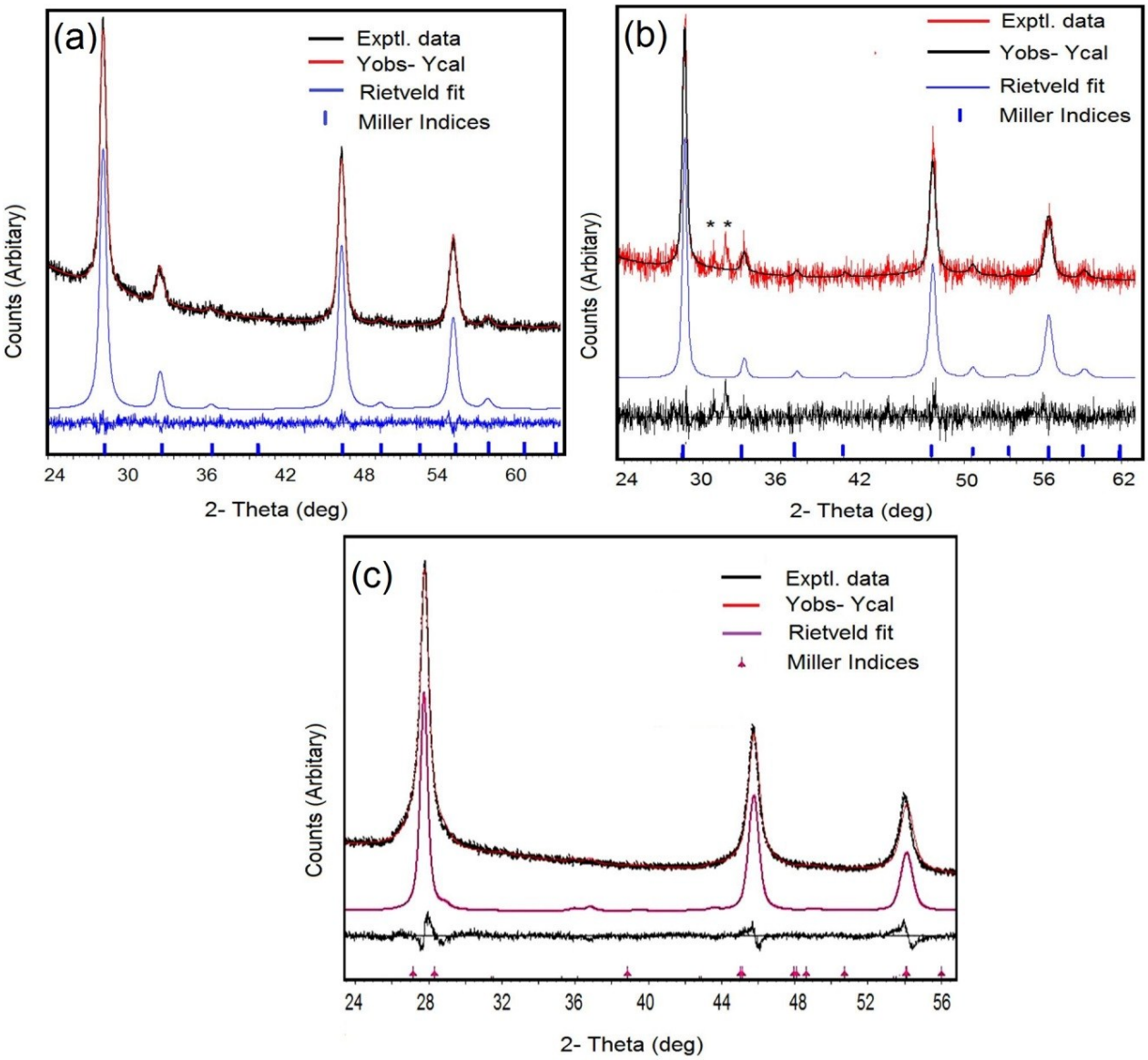

Figure S2: (a) and (b) are the Rietveld refinement of CFTS films deposited at 350 and 400 °C. (c) is the Rietveld refinement of CFTSe thin films deposited at 350 °C.

Table S1: Rietveld analysis of CFTS thin films deposited at 350 °C using CFTS (ICDD 00-053-0575 a = 5.4233). Rwp = 3.11, lattice constant a = 5.4261(6) Å.

h	k	l	d	2θ
1	1	0	3.82828	23.30030
0	1	1	3.82828	23.30030
1	1	1	3.12577	28.63786
0	2	0	2.70700	33.18699
0	0	2	2.70700	33.18699
1	2	0	2.42121	37.23970
0	2	1	2.42121	37.23970
0	1	2	2.42121	37.23970
2	1	0	2.42121	37.23970
1	2	1	2.21026	40.94553
1	1	2	2.21026	40.94553
2	1	1	2.21026	40.94553
2	2	0	1.91414	47.64074
0	2	2	1.91414	47.64074
2	2	1	1.80467	50.72824
0	3	0	1.80467	50.72824
0	0	3	1.80467	50.72824
1	2	2	1.80467	50.72824
2	1	2	1.80467	50.72824
3	1	0	1.71206	53.68519
0	1	3	1.71206	53.68519
0	3	1	1.71206	53.68519
1	3	0	1.71206	53.68519
1	1	3	1.63238	56.53389
3	1	1	1.63238	56.53389
1	3	1	1.63238	56.53389
2	2	2	1.56289	59.29181
0	2	3	1.50157	61.97298
2	3	0	1.50157	61.97298
3	2	0	1.50157	61.97298
0	3	2	1.50157	61.97298
2	3	1	1.44695	64.58891
3	1	2	1.44695	64.58891
1	3	2	1.44695	64.58891
2	1	3	1.44695	64.58891
1	2	3	1.44695	64.58891
3	2	1	1.44695	64.58891
0	0	4	1.35350	69.66219
0	4	0	1.35350	69.66219
1	4	0	1.31309	72.13493

0	1	4	1.31309	72.13493
4	1	0	1.31309	72.13493
0	4	1	1.31309	72.13493
2	3	2	1.31309	72.13493
3	2	2	1.31309	72.13493

Table S2: Rietveld analysis of CFTS thin films deposited at 400 °C using CFTS (ICDD 00-053-0575 a = 5.4233). Rwp = 4.61, lattice constant a = 5.414(4) Å.

h	k	l	d	2θ
0	0	2	5.41850	16.34580
0	1	1	4.85253	18.26770
1	1	0	3.83747	23.15939
1	1	2	3.13164	28.47864
0	1	3	3.00709	29.68472
0	2	0	2.71350	32.98337
0	0	4	2.70925	33.03659
0	2	2	2.42627	37.02153
2	1	1	2.36836	37.96088
1	1	4	2.21325	40.73491
2	1	3	2.01456	44.96065
0	1	5	2.01281	45.00167
2	2	0	1.91873	47.33916
0	2	4	1.91723	47.37857
2	2	2	1.80868	50.41383
0	0	6	1.80617	50.48904
0	3	1	1.78431	51.15177
3	1	0	1.71617	53.33955
3	1	2	1.63607	56.17541
1	1	6	1.63420	56.24519
0	3	3	1.61751	56.87819
2	1	5	1.61661	56.91280
2	2	4	1.56582	58.93703
0	2	6	1.50355	61.63710
3	2	1	1.49087	62.21933
0	1	7	1.48875	62.31760
3	1	4	1.44978	64.18962
3	2	3	1.38939	67.34077
0	3	5	1.38882	67.37218
0	4	0	1.35675	69.18728
0	0	8	1.35462	69.31130
0	4	2	1.31612	71.64552
2	2	6	1.31515	71.70660
4	1	1	1.30664	72.24684

Table S3: Rietveld analysis of CFTSe thin films deposited at 350 °C using CFTSe (ICDD: 00-027-0167, a = 5.6850 Å), Rwp = 2.56, lattice constant a = 5.713(0) Å.

h	k	l	d	2θ
1	1	0	4.02216	22.08222
1	1	1	3.28036	27.16219
0	2	0	2.84410	31.42860
0	0	4	2.83445	31.53838
0	2	2	2.54211	35.27763
2	1	1	2.48213	36.15913
1	1	4	2.31694	38.83680
2	1	3	2.11031	42.81715
0	1	5	2.10636	42.90144
2	2	0	2.01108	45.06256
0	2	4	2.00766	45.12353
2	2	2	1.89535	47.95965
0	0	6	1.88963	48.11386
0	3	1	1.87010	48.64885
3	1	0	1.79877	50.71142
3	1	1	1.71453	53.39470
2	1	5	1.69269	54.13931
2	2	4	1.64018	56.02222
0	2	6	1.57391	58.60447
3	2	1	1.56257	59.07185
0	1	7	1.55776	59.27216
3	1	4	1.51876	60.95367
3	2	3	1.45587	63.88925
0	3	5	1.45457	63.95308
0	4	0	1.42205	65.59634
0	0	8	1.41723	65.84792
0	4	2	1.37931	67.89933
2	2	6	1.37711	68.02304
4	1	1	1.36949	68.45367
2	1	7	1.36625	68.63848
3	3	0	1.34072	70.13483
1	1	8	1.33668	70.37849
3	3	2	1.30473	72.36931
3	1	6	1.30286	72.48959
4	1	3	1.29594	72.93848
3	2	5	1.29503	72.99844
4	2	0	1.27192	74.54668

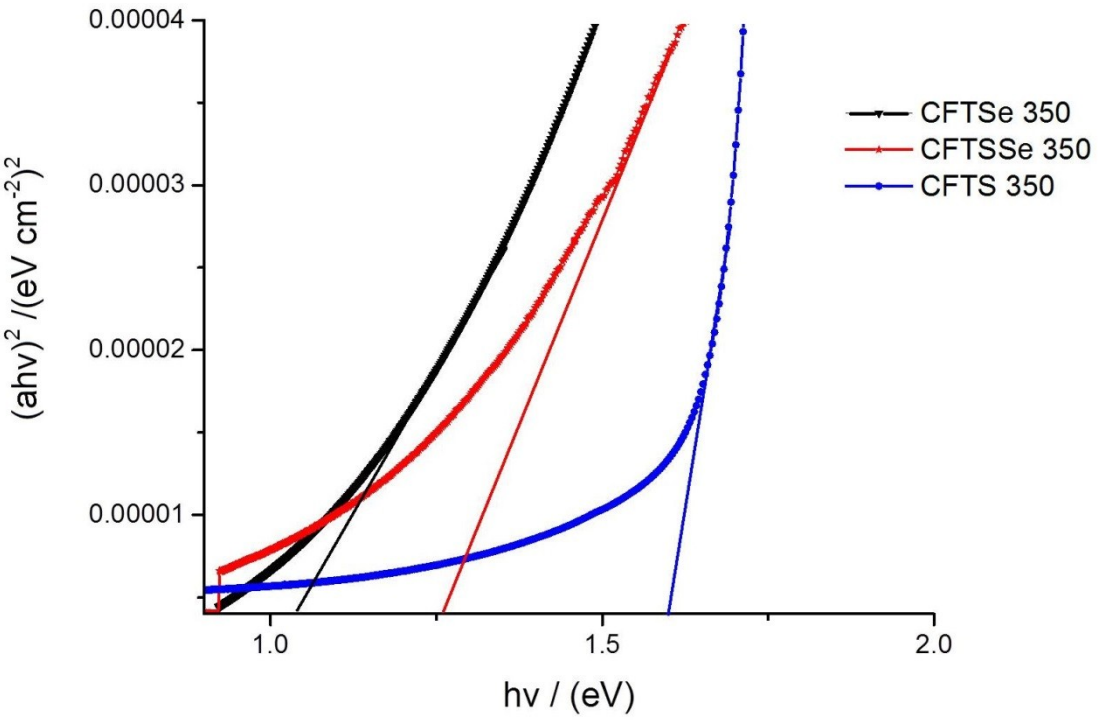

Figure S3: Tauc plot for the CFTS, CFTSSe and CFTSe thin films deposited at 350 °C.

Material	Intercept (a)	Slope (b)	BG (eV)	R^2
CFTS 350	4.67 x10^{-4}	2.95 x10^{-4}	1.58	0.8972
CFTSSe 350	2.86 x10^{-4}	2.27 x 10^{-4}	1.25	0.9382
CFTSe 350	6.36 x 10^{-4}	5.78 x 10^{-4}	1.10	0.9561

References

1. Revaprasadu, N.; Malik, M. A.; O'Brien, *South African Journal of Chemistry* **2004**, 57, 40-43.
2. Akhtar, M.; Akhter, J.; Malik, M. A.; O'Brien, P.; Tuna, F.; Raftery, J.; Helliwell, M. *Journal of Materials Chemistry* **2011,** *21* (26), 9737-9745.
3. Ramasamy, K.; Kuznetsov, V. L.; Gopal, K.; Malik, M. A.; Raftery, J.; Edwards, P. P.; O'Brien, P.,. *Chemistry of Materials* **2013,** *25* (3), 266-276.
4. Trofimov ,B. A; Artem'Ev, A. V.; Gusarova, N. K.; Malysheva, S. F.; Fedorov, S. V.; Kazheva, O. N.; Alexandrov G. G.; and. Dyachenko O. A.; *Synthesis*, 2009, 3332-3338.