SUPPORTING INFORMATION

Vegard relation and Raman band reference data generated from bulk crystals of kesterite phase composition series $Cu_2ZnSnS_{4x}Se_{4-4x}$ (CZTSSe $0 \leq x \leq 1$)

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Author Contributions
The manuscript was written with contributions from all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

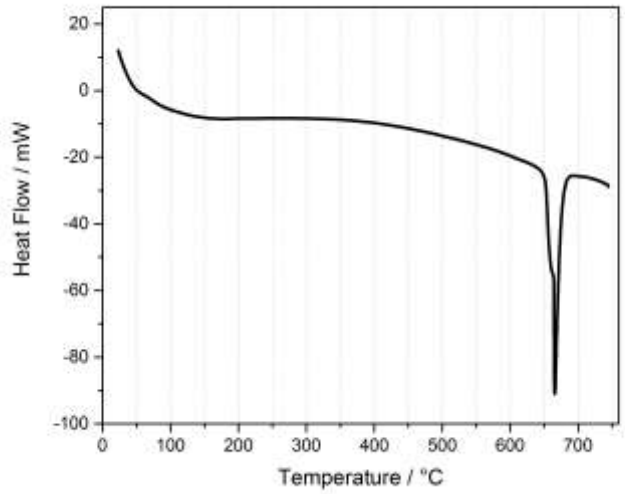


Figure S1. DSC heat flow (during heating at 5°C/min) against temperature for 1:1 mole ratio NaCl:KCl; the large endotherm near 660°C represents melting of the eutectic mixture.

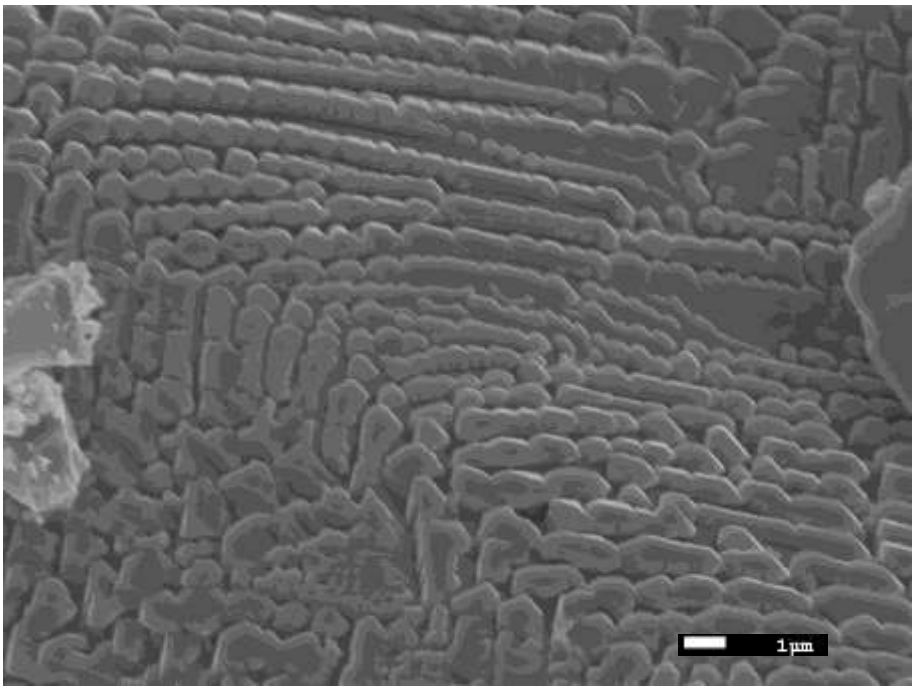


Figure S2. SEM image of CZTSSe (x = 0.5) feedstock showing crystal grains about 1 µm in size.

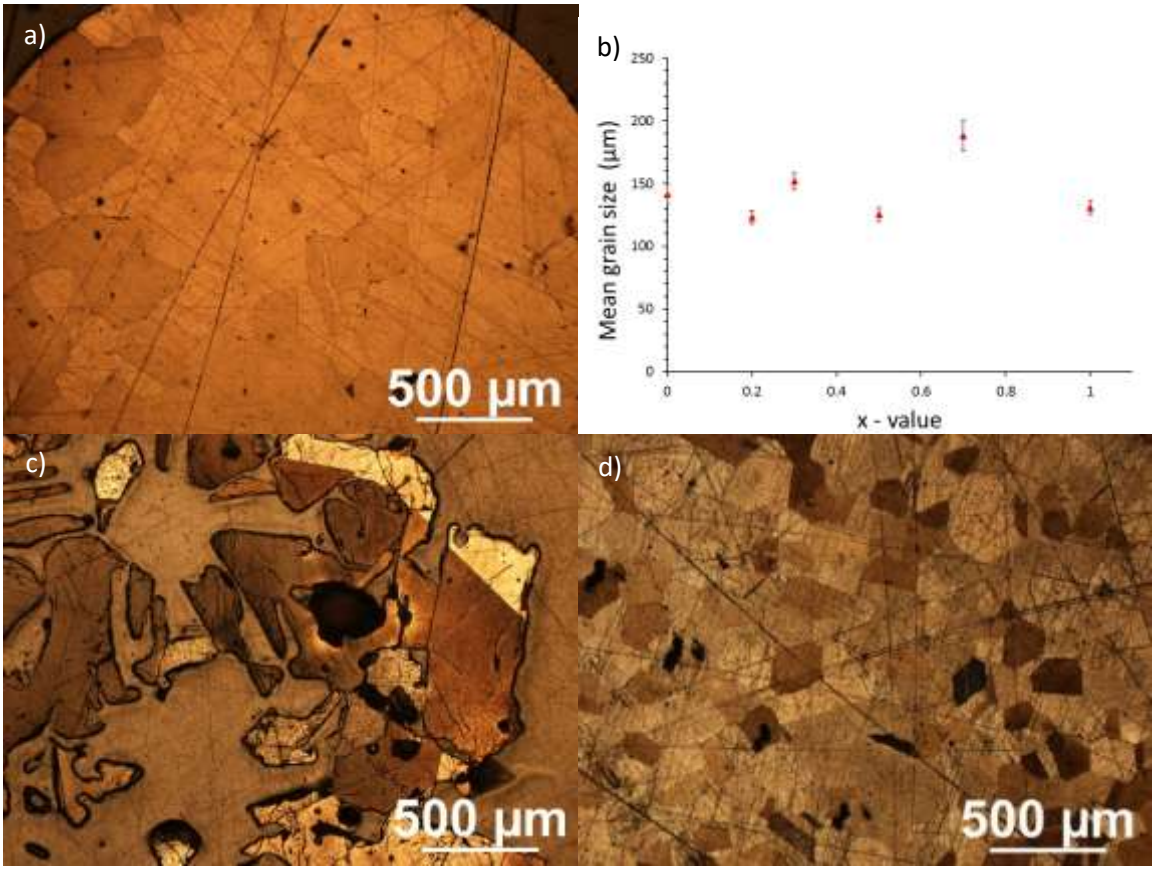


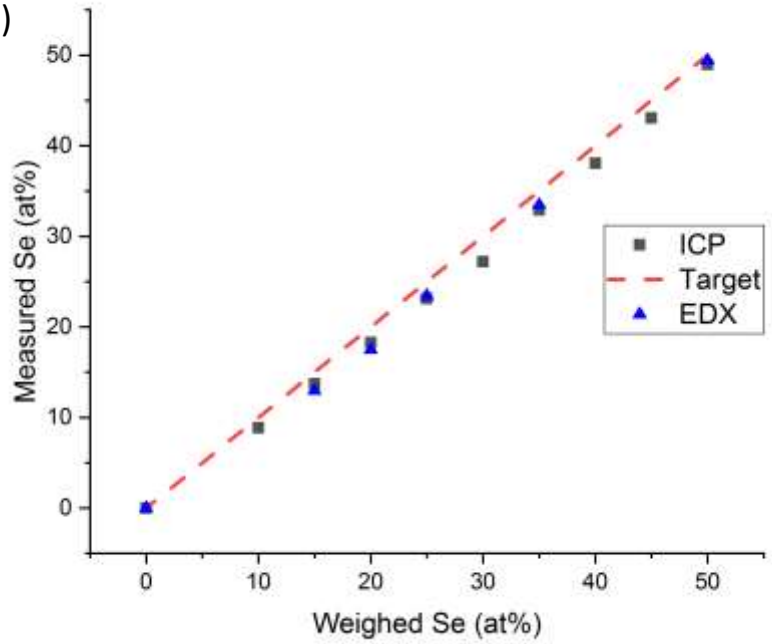
Figure S3. (a) Micrograph of polished surface of compact crystallised $Cu_2ZnSnS_{4x}Se_{4-4x}$ (x = 0.3) deposit formed on walls of growth tube from crystallisation in NaCl/KCl mix. (b) Mean grain size (error is standard deviation) in the compact deposits plotted against x-value. c) Micrograph showing free grains of crystallised CZTS (x = 1) nucleated within the liquid NaCl/KCl mix. d) Micrograph of compact crystallised CZTS (x = 1) formed on seed plate.

***x*-value**	**Cu At%**	**Zn At%**	**Sn At%**	**S At%**	**Se At%**	**N**	**Cu/ (Zn+Sn)**	**Cu/Zn**	**Cu/Sn**	**Zn/Sn**
Feedstock - Weighed										
0	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	0	50 ± 0.01		1	2	2	1
0.1	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	5 ± 0.01	45 ± 0.01		1	2	2	1
0.2	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	10 ± 0.01	40 ± 0.01		1	2	2	1
0.3	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	15 ± 0.01	35 ± 0.01		1	2	2	1
0.4	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	20 ± 0.01	30 ± 0.01		1	2	2	1
0.5	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	25 ± 0.01	25 ± 0.01		1	2	2	1
0.6	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	30 ± 0.01	20 ± 0.01		1	2	2	1
0.7	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	35 ± 0.01	15 ± 0.01		1	2	2	1
0.8	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	40 ± 0.01	10 ± 0.01		1	2	2	1
1	25 ± 0.01	12.5 ± 0.01	12.5 ± 0.01	50 ± 0.01	0		1	2	2	1

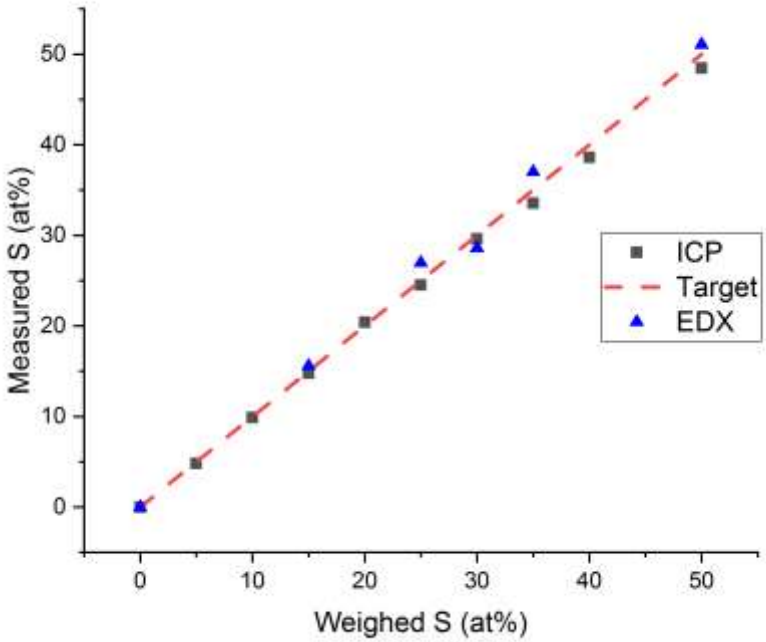
Feedstock - EDX										
0	27.3 ± 1.0	12.6 ± 0.7	15.8 ± 1.2	7.3 ± 1.0	37.3 ± 1.0	9	0.961	2.167	1.728	0.797
0.1	27.3 ± 0.7	12.2 ± 0.7	12.0 ± 0.7	20.8 ± 1.4	27.8 ± 0.8	7	1.128	2.238	2.275	1.017
0.3	28.1 ± 0.8	11.6 ± 0.7	15.8 ± 1.3	26.0 ± 0.8	18.6 ± 0.7	12	1.026	2.422	1.778	0.734
0.5	28.3 ± 0.4	13.0 ± 0.5	14.0 ± 1.2	28.5 ± 0.6	16.1 ± 0.5	9	1.048	2.177	2.021	0.929
0.6	28.0 ± 1.2	14.29 ± 0.21	13.3 ± 1.1	32.8 ± 0.6	11.7 ± 1.9	2	1.015	1.959	2.105	1.074
0.7	23.3 ± 2.5	20.8 ± 2.5	9.9 ± 0.3	42.3 ± 1.2	3.7 ± 0.3	2	0.759	1.120	2.354	2.101
0.9	25.4 ± 1.3	17.4 ± 1.5	10.90 ± 0.13	46.3 ± 0.3	0	2	0.898	1.460	2.330	1.596
1	30.1 ± 0.3	12.7 ± 0.4	11.3 ± 0.3	0	45.9 ± 0.5	4	1.254	2.370	2.664	1.124
Crystallised-EDX										
0	25.48 ± 0.23	12.11 ± 0.25	13.00 ± 0.11	0	49.41 ± 0.29	9	1.014	2.104	1.960	0.931
0.3	24.7 ± 0.3	13.65 ± 0.20	12.62 ± 0.17	15.60 ± 0.28	33.45 ± 0.29	6	0.940	1.809	1.957	1.081
0.5	24.97 ± 0.20	11.89 ± 0.16	12.74 ± 0.14	26.96 ± 0.23	23.43 ± 0.15	7	1.013	2.100	1.959	0.933
0.6	27.7 ± 1.2	13.8 ± 0.6	12.4 ± 0.8	28.6 ± 0.4	17.5 ± 0.8	3	1.057	2.007	2.233	1.112
0.7	24.82 ± 0.27	12.00 ± 0.20	13.17 ± 0.09	37.02 ± 0.20	12.98 ± 0.24	8	0.986	2.068	1.884	0.911
1	24.58 ± 0.15	11.61 ± 0.18	12.75 ± 0.11	51.06 ± 0.26	0	11	1.009	2.117	1.927	0.910
Crystallised-ICP-OES										
0	27.11 ± 0.10	11.44 ± 0.05	12.480 ± 0.027	0	49.0 ± 0.4	3	1.132	2.368	2.171	0.917
0.1	27.54 ± 0.07	12.278 ± 0.007	12.318 ± 0.016	4.808 ± 0.026	43.05 ± 0.22	3	1.119	2.243	2.236	0.996
0.2	26.653 ± 0.031	13.344 ± 0.031	12.06 ± 0.021	9.87 ± 0.07	38.1 ± 0.1	3	1.049	1.997	2.210	1.106
0.3	27.24 ± 0.06	12.961 ± 0.006	12.120 ± 0.022	14.78 ± 0.05	32.91 ± 0.15	3	1.085	2.101	2.247	1.069
0.4	27.29 ± 0.04	12.99 ± 0.04	12.139 ± 0.027	20.39 ± 0.12	27.20 ± 0.12	3	1.085	2.100	2.247	1.069
0.5	27.75 ± 0.04	12.452 ± 0.009	12.186 ± 0.022	24.50 ± 0.23	23.11 ± 0.06	3	1.126	2.228	2.277	1.021
0.6	27.579 ± 0.009	12.398 ± 0.014	12.137 ± 0.025	29.6 ± 0.3	18.27 ± 0.08	3	1.124	2.224	2.272	1.021
0.7	28.171 ± 0.011	12.28 ± 0.04	12.29 ± 0.03	33.5 ± 0.4	13.7 ± 0.1	3	1.146	2.294	2.292	0.999
0.8	27.883 ± 0.026	12.41 ± 0.03	12.25 ± 0.03	38.6 ± 0.6	8.86 ± 0.14	3	1.130	2.246	2.276	1.013
1	26.74 ± 0.19	12.66 ± 0.06	12.138 ± 0.03	48.46 ± 0.13	0	3	1.07	2.111	2.202	1.043

Table S1. Elemental determination of the feedstock $Cu_2ZnSnS_{4x}Se_{4-4x}$ and solid solutions crystallised in NaCl/KCl mix, with compositions from EDX (uncertainty is standard deviation, with number of measurements for each composition $2 \leq N \leq 12$ for feedstock and $3 \leq N \leq 11$ for crystallised) and from ICP-OES (uncertainty is standard deviation of concentrations determined from 3 emission wavelengths in each case, hence N = 3). Weighed proportions of elements prior to synthesis are also shown, with uncertainty based on all weighed quantities being within 1 mg of target mass.

a)


Measured Se (at%)
Weighed Se (at%)
ICP
Target
EDX
0
10
20
30
40
50

b)


Measured S (at%)
Weighed S (at%)
ICP
Target
EDX
0
10
20
30
40
50

c)

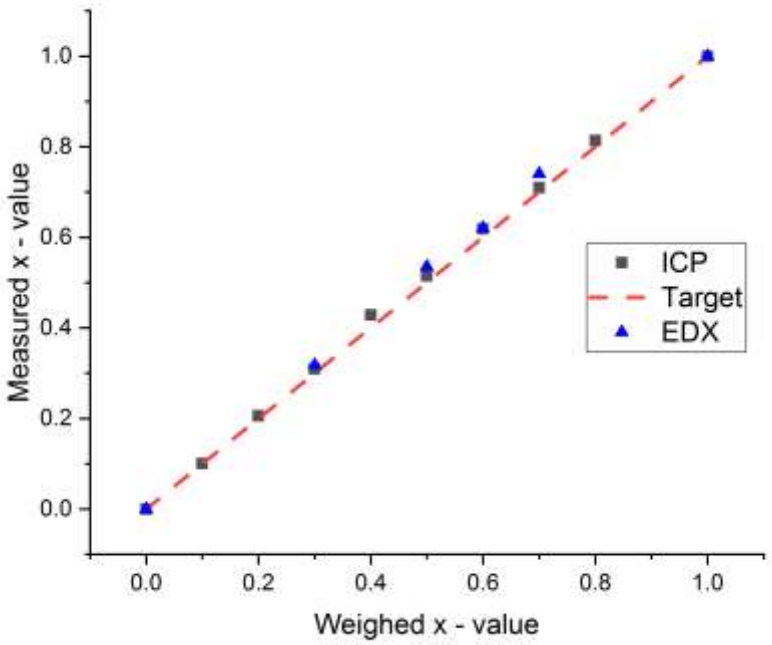
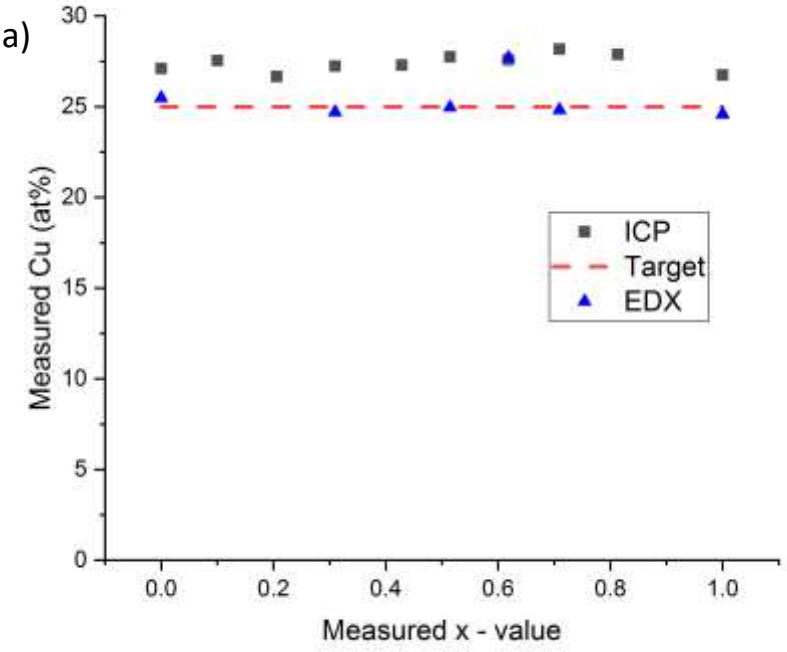
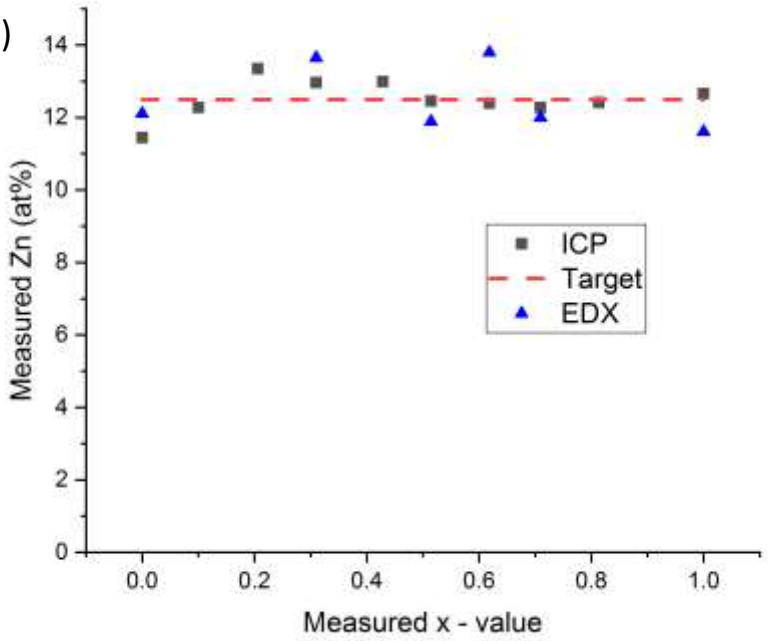


Figure S4. EDX and ICP-OES results for samples in the crystallised CZTSSe series showing a) Se quantities b) S quantities and c) measured *x* – values, compared to weighed quantities. There is reasonable agreement between the results from ICP-OES and EDX, and both correspond well to the target quantities. This suggests that for samples prepared in this way, both EDX and ICP-OES may be employed to accurately determine the anion ratios

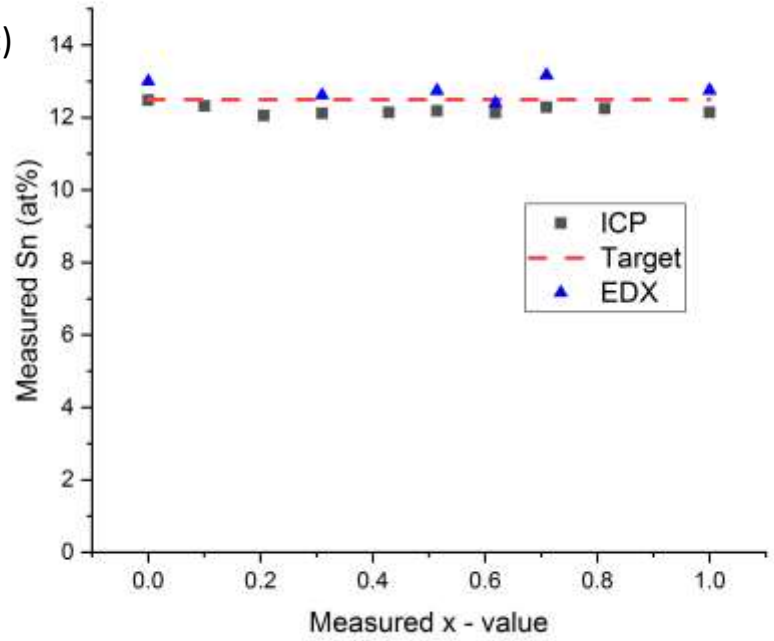
a)



b)


Measured Zn (at%)
Measured x - value
ICP
Target
EDX
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0

c)


Measured Sn (at%)
Measured x - value
ICP
Target
EDX
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0

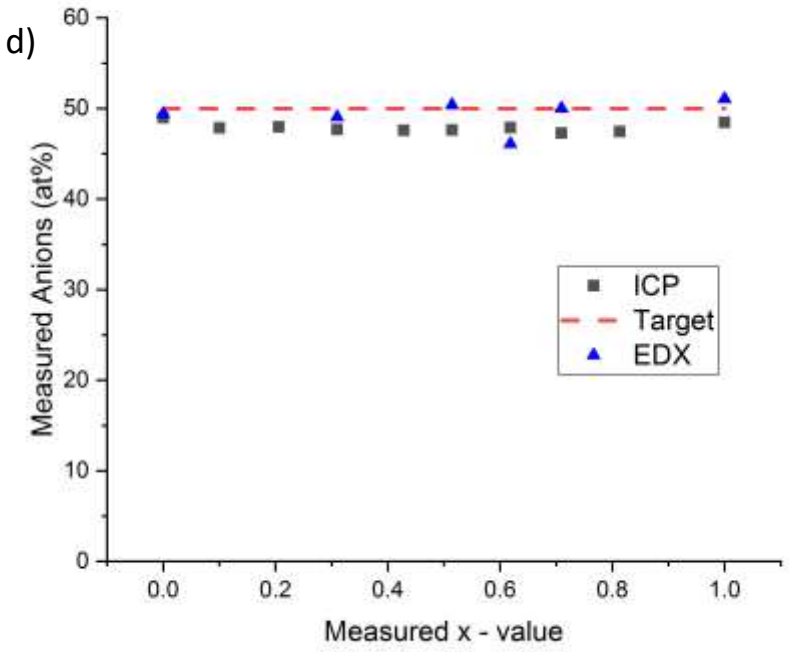
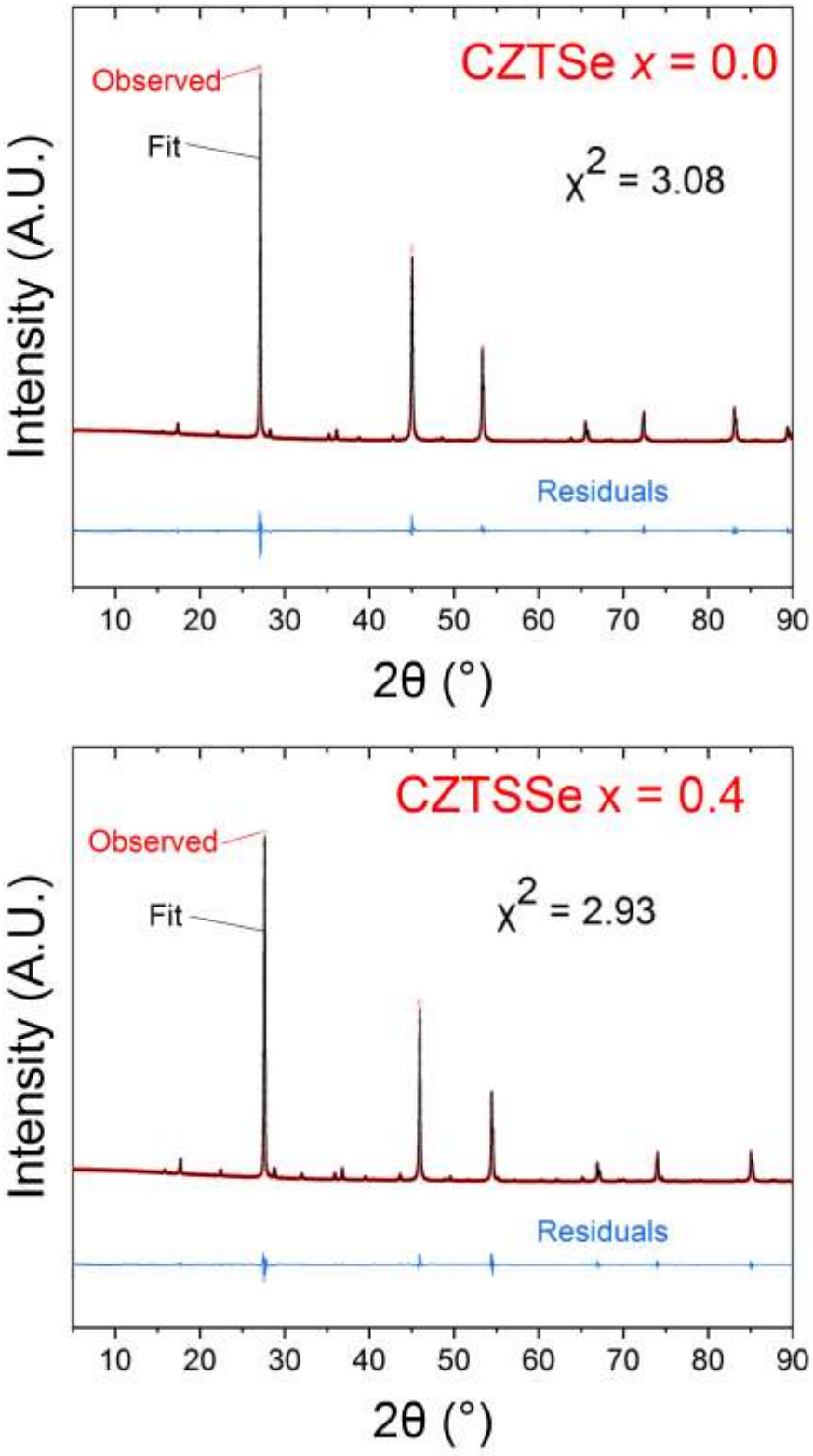


Figure S5. EDX and ICP-OES results for samples in the crystallised CZTSSe series showing a) Cu quantities, b) Zn quantities, c) Sn quantities and d) total anion quantities. Again, there is clear agreement between the two methods, and agreement with the weighed quantities. However there is also a clear discrepancy in the copper quantities.

Rietveld Refinement Methodology

Refinement was carried out by refining, then fixing, parameters in the following order:

1. Refine scale factor and first 6 polynomial coefficients
2. Refine lattice parameters and instrument zero
3. Refine atomic (anion only) positions
4. Fix atomic positions and refine overall B_Iso
5. Refine both atomic positions and B_Iso
6. Refine 7th background coefficient
7. Refine peak shape parameters and all 4 asymmetry parameters
8. Refine 8th background coefficient


CZTSe x = 0.0
Observed
Fit
χ2 = 3.08
Residuals
Intensity (A.U.)
10
20
30
40
50
60
70
80
90
2θ (°)
CZTSSe x = 0.4
Observed
Fit
χ2 = 2.93
Residuals
Intensity (A.U.)
10
20
30
40
50
60
70
80
90
2θ (°)

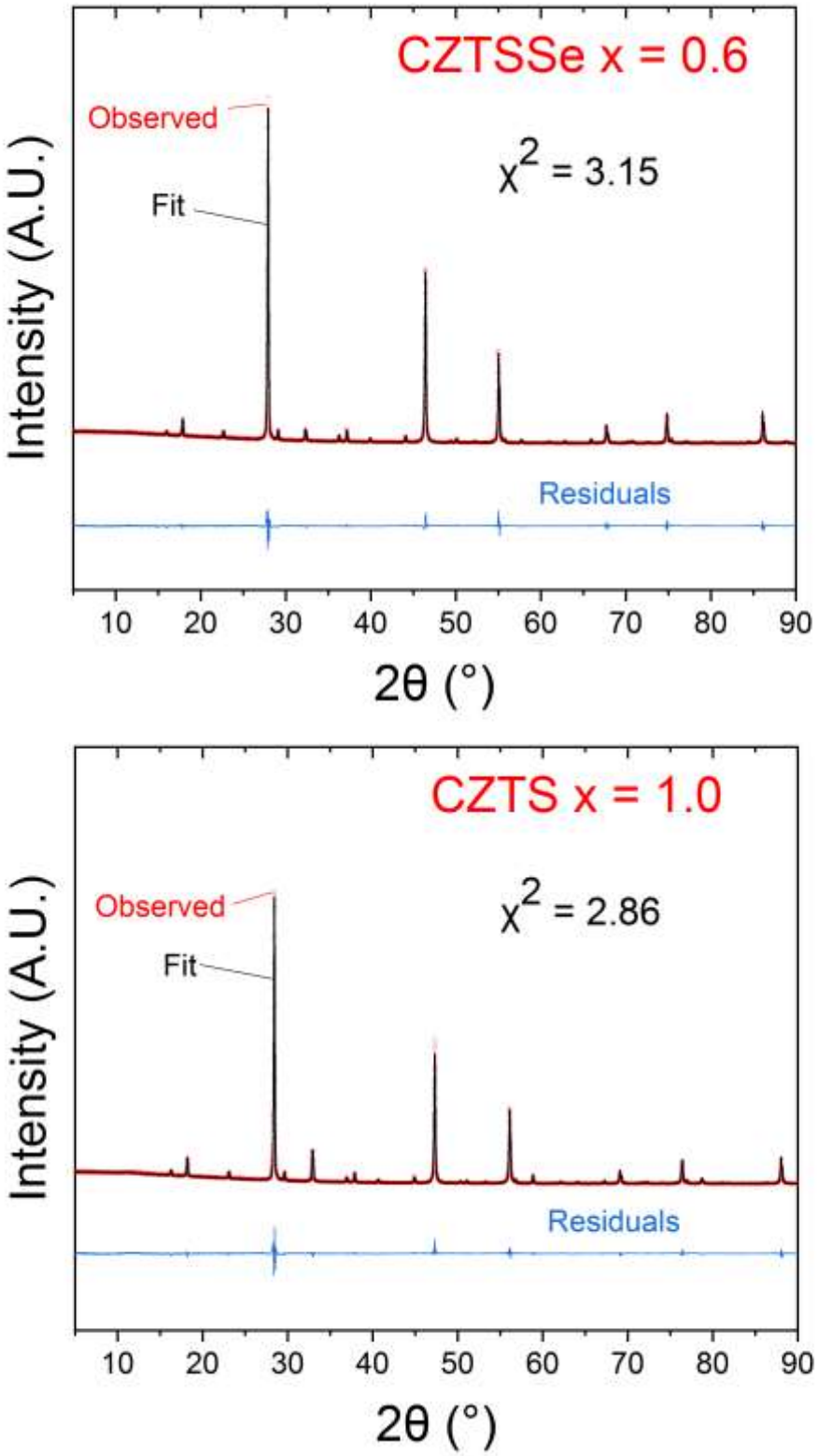


Figure S6. Observed and fitted XRD patterns (with residuals) for the crystallised CZTSSe samples where a) $x = 0$, b) $x = 0.4$, c) $x = 0.6$, d) $x = 1$. The observed x-ray data are shown with red circles, the fit with a black line, and residuals with a blue line. Values of χ^2 and Bragg R-factor (R_B) are shown on the plots.

x - value (Weighed):	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1
χ^2	3.08	3.47	3.36	2.74	2.93	2.64	3.15	2.66	2.96	2.86
R_p	12.3	14.0	13.1	13.2	12.8	14.0	13.5	12.8	14.6	14.1
R_{wp}	13.1	14.1	13.9	13.4	13.3	13.7	13.9	13.3	14.4	14.2
R_{exp}	7.46	7.59	7.56	8.12	7.79	8.43	7.81	8.14	8.38	8.38
R_{Bragg}	4.18	4.26	3.94	4.30	3.98	3.46	3.89	3.43	5.78	3.98

Table S2. Conventional Rietveld parameters for refinement of crystallised solid solutions series, where χ^2 refers to the chi-square statistic, R_p refers to the profile residual, R_{wp} refers to the weighted profile residual, R_{exp} refers to the expected profile residual, and R_{Bragg} refers to the Bragg residual.

x – value (Measured):	**0**	**0.1004(5)**	**0.2059(14)**	**0.3099(10)**	**0.4285(24)**
Lattice parameters (Å)					
a	5.69258(3)	5.67077(3)	5.64406(3)	5.61520(3)	5.58530(3)
c	11.34351(8)	11.29954(8)	11.24646(8)	11.1876(8)	11.13394(7)
Anion positions					
x	0.765(5)	0.7574(11)	0.7544(7)	0.7567(9)	0.7505(6)
y	0.755(4)	0.7645(8)	0.7677(5)	0.7669(7)	0.7710(4)
z	0.87047(16)	0.87033(17)	0.87049(18)	0.87003(18)	0.86964(19)
B_{Iso} (Å^2)	0.953(19)	0.941(21)	1.184(22)	0.996(21)	0.949(21)
x – value (Measured):	**0.514(5)**	**0.618(6)**	**0.709(8)**	**0.813(12)**	**1**
Lattice parameters (Å)					
a	5.56237(4)	5.53041(3)	5.50522(3)	5.47855(3)	5.43170(3)
c	11.09142(9)	11.03185(8)	10.98109(7)	10.92823(7)	10.83919(8)
Anion positions					
x	0.7527(7)	0.7518(7)	0.7503(7)	0.75040(8)	0.7674(15)
y	0.7701(5)	0.7711(5)	0.7735(5)	0.7727(6)	0.7551(17)
z	0.86993(21)	0.86949(22)	0.86992(24)	0.86973(28)	0.8701(3)
B_{Iso} (Å^2)	1.298(21)	1.011(22)	1.053(22)	0.677(23)	0.819(22)

Table S3. Refined lattice parameters, anion positions and B_{Iso} parameter for crystallised CZTSSe solid solutions. x – value is given in terms of the quantity S/(Se+S) measured via ICP-OES for a given sample.

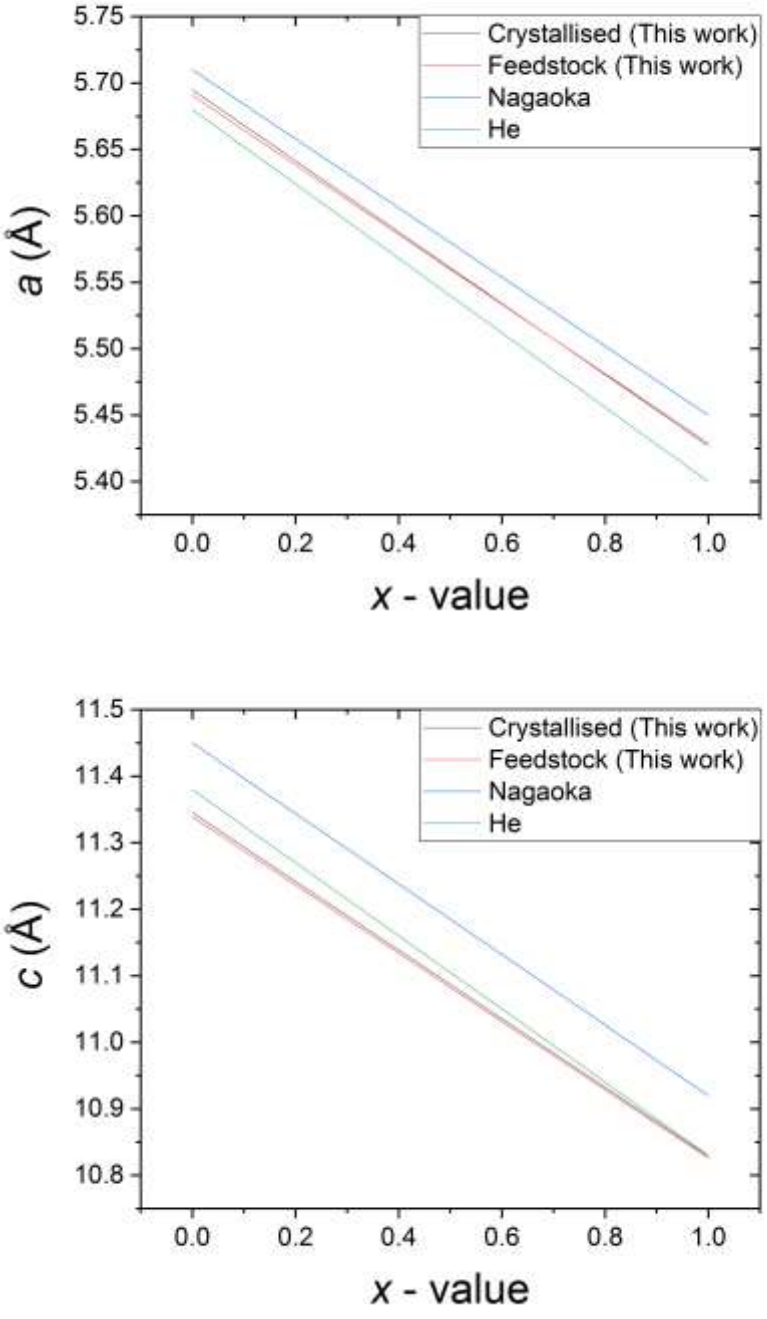


Figure S7. Comparison of the lattice parameters *a* (top) and *c* (bottom) for $Cu_2ZnSnS_{4x}Se_{4-4x}$ as determined from this work (both as-synthesised feedstock and crystallised material), and from Nagaoka *et al.*[7] and He *et al.*[10]. The values of Nagaoka *et al.* are systematically higher than our own. For the values of He *et al.*, the *a* values are lower than ours while the *c* values are higher, but the difference is composition-dependent.

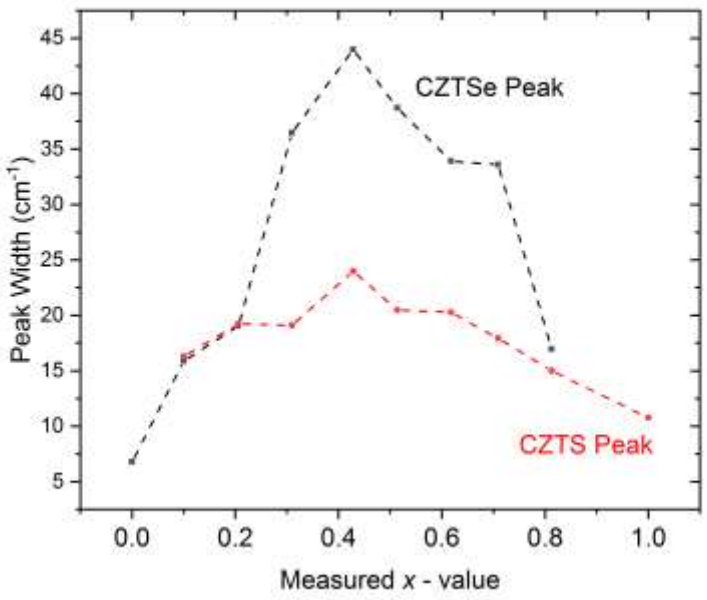


Figure S8. Plot of widths of both CZTSe-like and CZTS-like peaks observed in Raman spectra taken across the composition range $0 \leq x \leq 1$ for the crystallised samples. Both peaks are similarly narrow in the vicinity of $x = 0$ and $x = 1$ but both broaden at intermediate compositions, with the CZTSe peak broadening more dramatically than the CZTS peak.