Supplementary information for

Characterization of Cu_2ZnSnS_4 particles obtained by the hot-injection method

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Calculated PXRD patterns

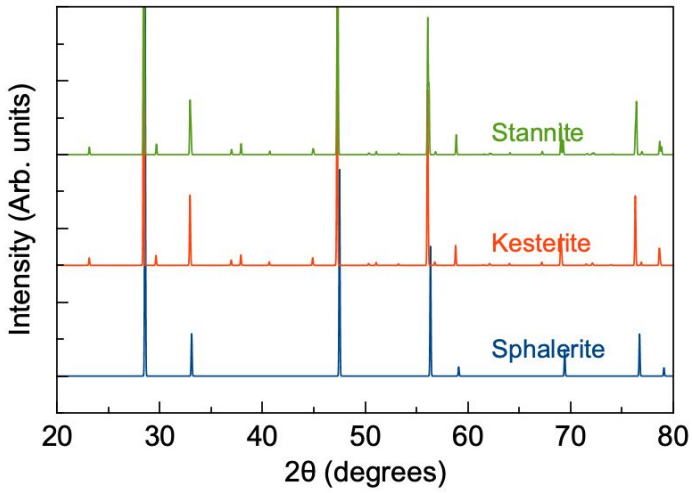

Figure S1: Calculated diffraction patterns for the stannite, kesterite and sphalerite structures, illustrated in Figure 1.

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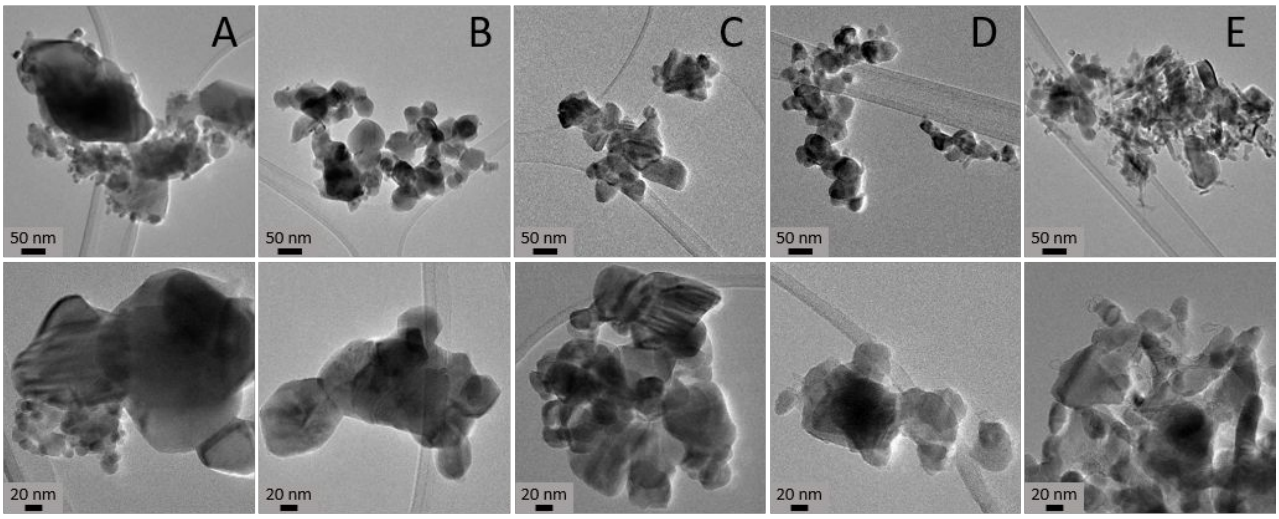


Figure S2: TEM images of annealed samples A to E at different magnification.

Rietveld results

R_{Bragg}	6.72%
R_F	4.42%
a (Å)	5.433(3)
c (Å)	10.79(1)
Y	0.618(5)
Crystallite size	9.1 nm

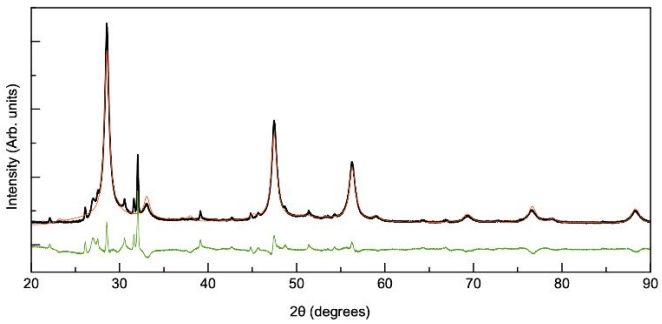


Figure S3: Rietveld refinement of laboratory data obtained for as-synthesized sample A.

R_{Bragg}	6.17%
R_F	4.58%
a (Å)	5.434(2)
c (Å)	10.81(1)
Y	0.436(7)
Crystallite size	12.8 nm

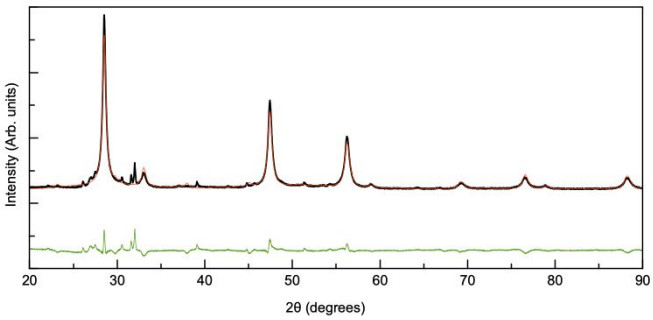


Figure S4: Rietveld refinement of laboratory data obtained for as-synthesized sample B.

R_{Bragg}	6.02%
R_F	4.66%
a (Å)	5.433(1)
c (Å)	10.82(1)
Y	0.26(1)
Crystallite size	21.0 nm

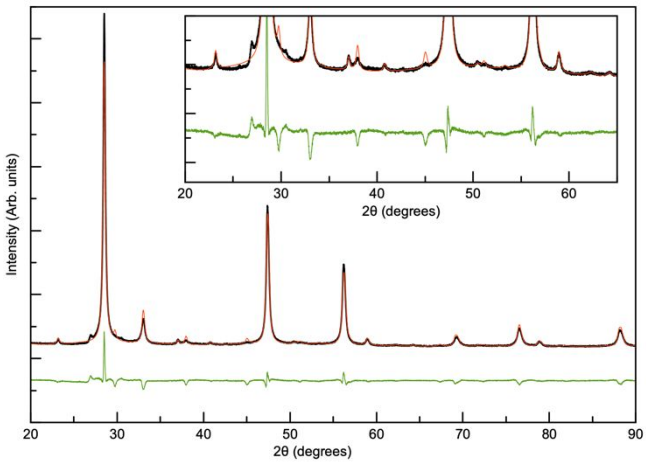


Figure S5: Rietveld refinement of laboratory data obtained for as-synthesized sample C. Inset shows a magnification of the difference curve.

R_{Bragg} (CZTS)	5.79%
R_F (CZTS)	8.51%
a (Å) (CZTS)	5.443(2)
c (Å) (CZTS)	10.77(1)
Y (CZTS)	0.36(4)
Crystallite size (CZTS)	15.2 nm
Weight percent (CZTS)	35.16%
R_{Bragg} (Sphalerite)	2.90%
R_F (Sphalerite)	3.25%
a (Å) (Sphalerite)	5.425(1)
Y (Sphalerite)	0.19(1)
Crystallite size (Sphalerite)	29 nm
Weight percent (Sphalerite)	64.84%

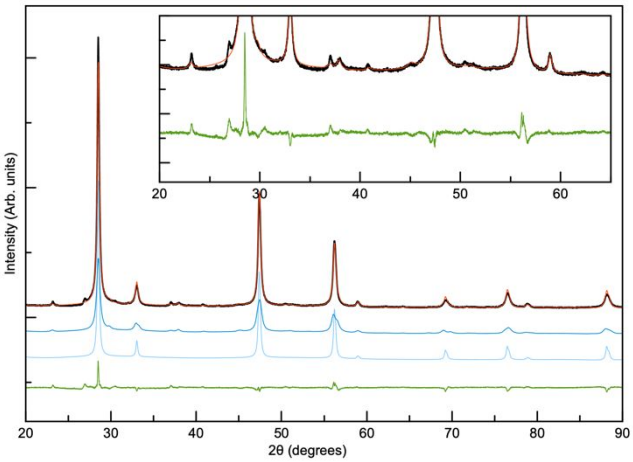


Figure S6: Rietveld refinement of laboratory data obtained for as-synthesized sample C, fitting with the kesterite CZTS and sphalerite ZnS structure. The contributions to the fit are shown in dark blue (kesterite) and light blue (sphalerite). Inset shows a magnification of the difference curve.

R_{Bragg}	5.96%
R_F	4.66%
a (Å)	5.436(1)
c (Å)	10.79(1)
Y	0.493(4)
Crystallite size	11.4 nm

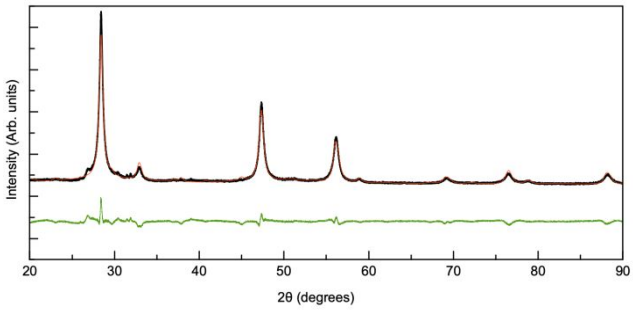


Figure S7: Rietveld refinement of laboratory data obtained for as-synthesized sample D.

R_{Bragg}	6.12%
R_F	4.98%
a (Å)	5.433(1)
c (Å)	10.82(1)
Y	0.257(2)
Crystallite size	21.9 nm

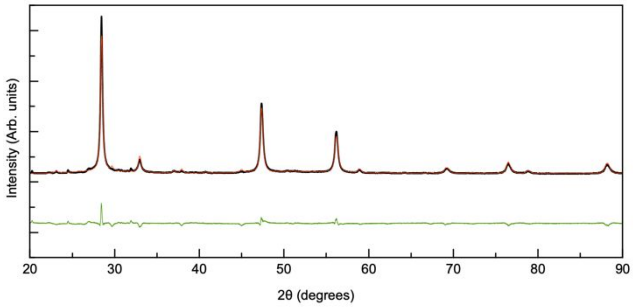
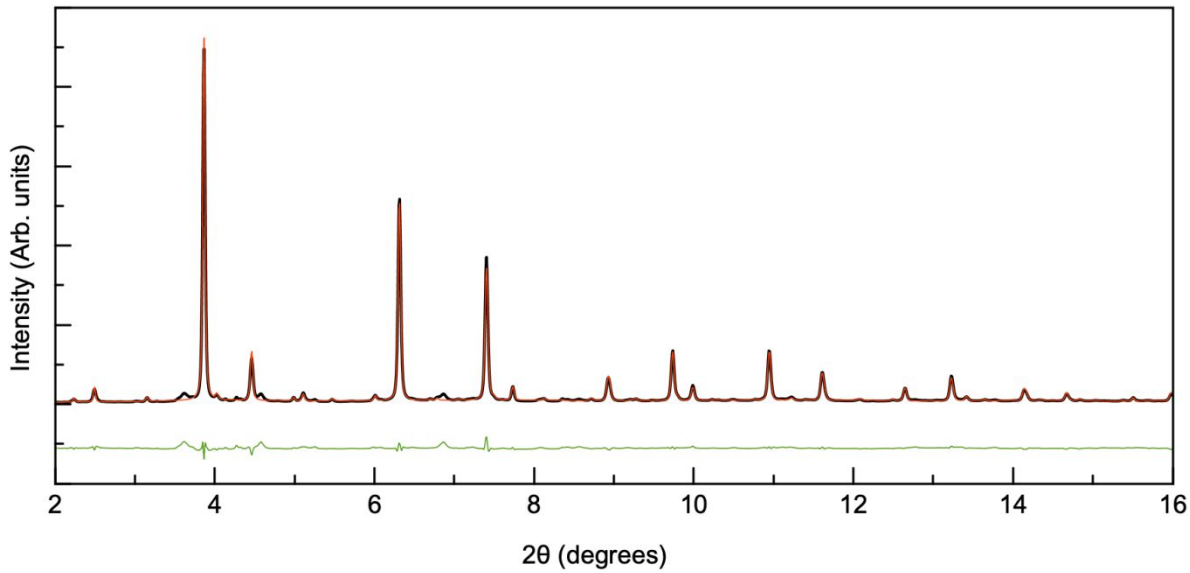


Figure S8: Rietveld refinement of laboratory data obtained for as-synthesized sample E.



R_{Bragg}	6.39%	B_{iso}, Cu 2a	0.7(2) Å^2	x_S	0.77(3)
R_F	9.66%	B_{iso}, Cu 2c	0.8(3) Å^2	y_S	0.74(2)
a (Å)	5.433(1)	B_{iso}, Zn 2d	1.2(3) Å^2	z_S	0.872(9)
c (Å)	10.838(5)	B_{iso}, Sn 2b	0.7(2) Å^2		
Y	0.0177(4)	B_{iso}, S 8g	0.3(2) Å^2		
U	-0.099(1)	Occ, Cu 2c	0.95(2)		
V	0.021(1)	Occ, Sn 2b	0.95(2)		

Figure S9: Rietveld refinement of synchrotron data obtained for annealed sample A.

R_{Bragg}	3.80%	B_{iso}, Cu 2a	0.9(2) Å^2	x_S	0.77(2)
R_F	8.89%	B_{iso}, Cu 2c	0.7(2) Å^2	y_S	0.74(2)
a (Å)	5.433(1)	B_{iso}, Zn 2d	1.3(2) Å^2	z_S	0.871(6)
c (Å)	10.834(3)	B_{iso}, Sn 2b	0.7(2) Å^2		
Y	0.0190(8)	B_{iso}, S 8g	0.7(2) Å^2		
U	-0.083(9)	Occ, Cu 2c	0.92(2)		
V	0.019(7)	Occ, Sn 2b	0.94(2)		

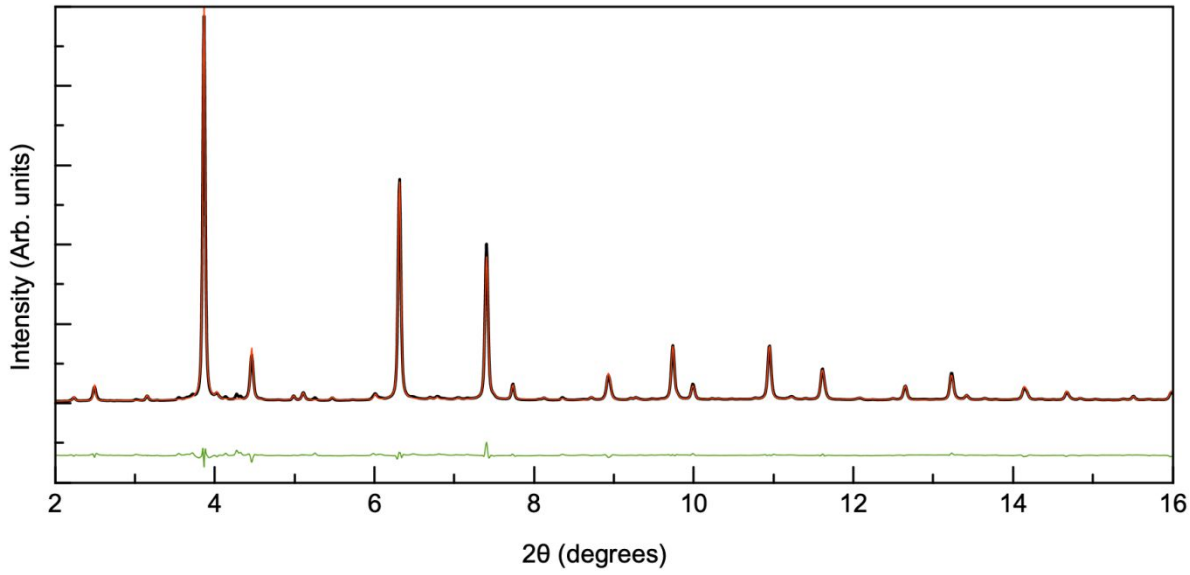
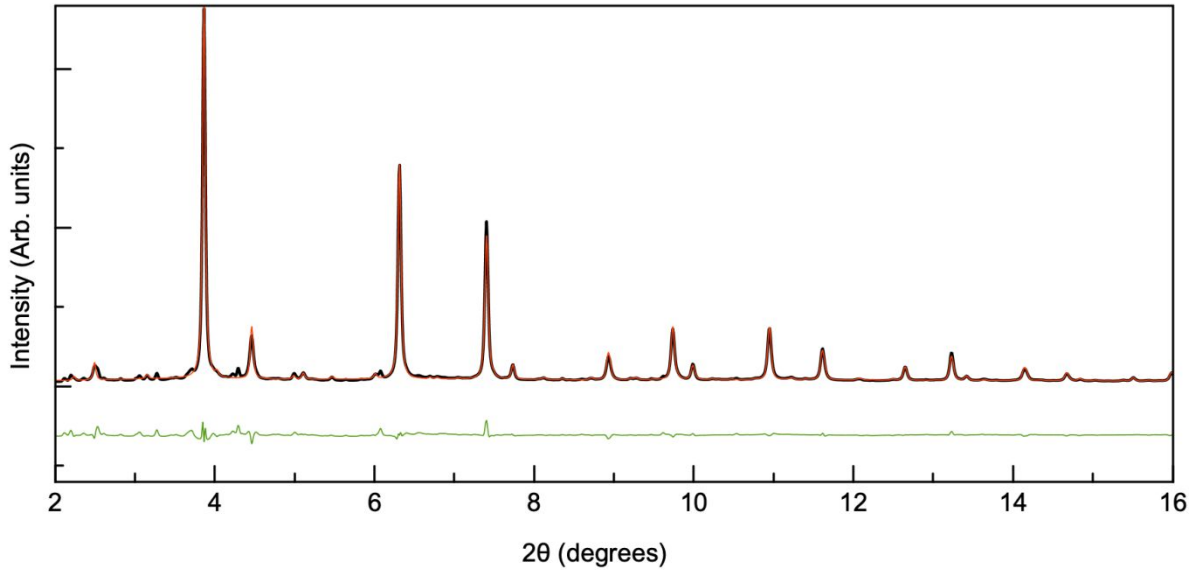
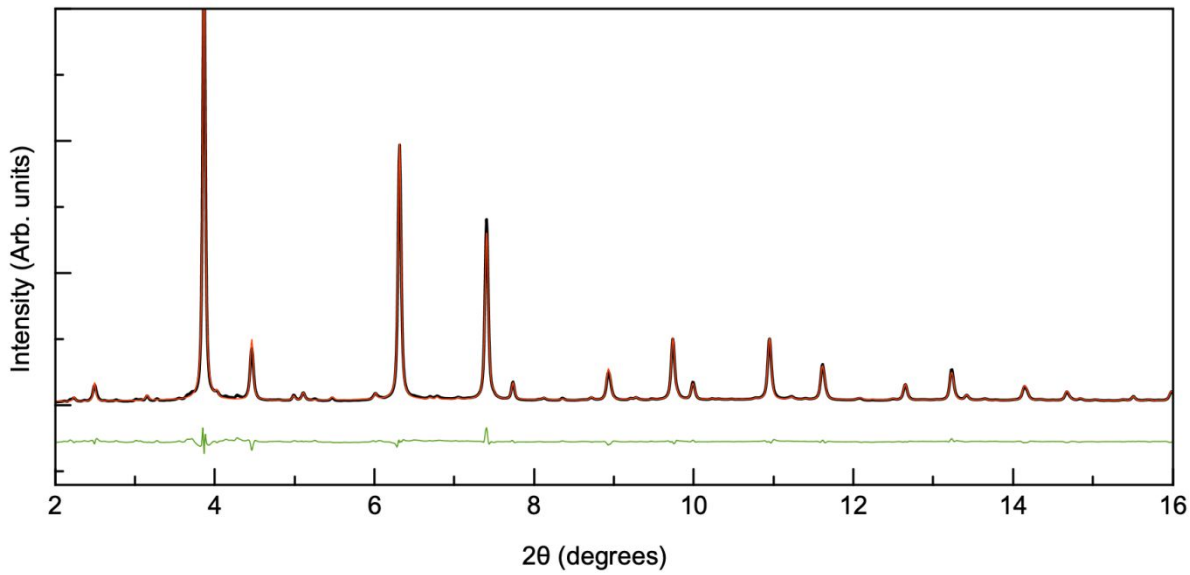


Figure S10: Rietveld refinement of synchrotron data obtained for annealed sample B.



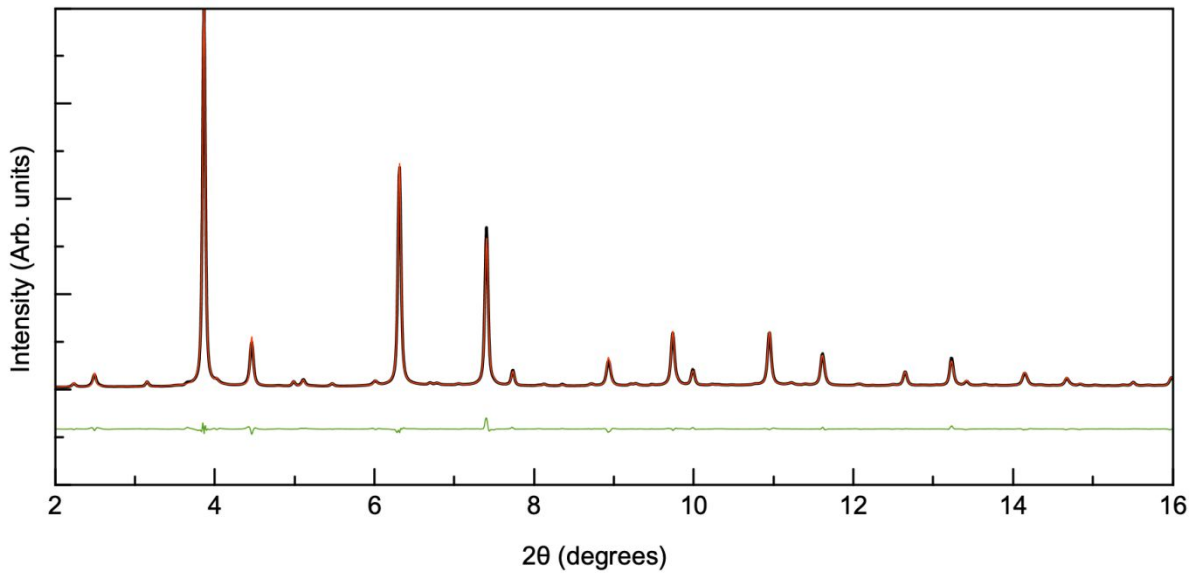
R_{Bragg}	4.63%	B_{iso}, Cu 2a	0.6(3) Å^2	x_S	0.77(4)
R_F	5.81%	B_{iso}, Cu 2c	0.4(3) Å^2	y_S	0.73(2)
a (Å)	5.433(2)	B_{iso}, Zn 2d	1.5(4) Å^2	z_S	0.87(1)
c (Å)	10.837(7)	B_{iso}, Sn 2b	1.1(3) Å^2		
Y	0.0331(4)	B_{iso}, S 8g	0.4(2) Å^2		
U	-0.0233(2)	Occ, Cu 2c	0.95(2)		
V	0.011(1)	Occ, Sn 2b	0.96(1)		

Figure S11: Rietveld refinement of synchrotron data obtained for annealed sample C.



R_{Bragg}	2.61%	B_{iso}, Cu 2a	0.7(2) Å^2	x_S	0.77(2)
R_F	4.44%	B_{iso}, Cu 2c	0.6(2) Å^2	y_S	0.75(2)
a (Å)	5.433(1)	B_{iso}, Zn 2d	1.5(2) Å^2	z_S	0.87(1)
c (Å)	10.840(3)	B_{iso}, Sn 2b	0.8(1) Å^2		
Y	0.0291(2)	B_{iso}, S 8g	0.5(1) Å^2		
U	-0.025(1)	Occ, Cu 2c	0.933(5)		
V	0.0128(8)	Occ, Sn 2b	0.940(8)		

Figure S12: Rietveld refinement of synchrotron data obtained for annealed sample D.



R_{Bragg}	2.70%	B_{iso}, Cu 2a	0.7(2) Å^2	x_S	0.78(2)
R_F	4.90%	B_{iso}, Cu 2c	0.6(1)Å^2	y_S	0.74(1)
a (Å)	5.433(1)	B_{iso}, Zn 2d	1.4(1) Å^2	z_S	0.87(1)
c (Å)	10.837(3)	B_{iso}, Sn 2b	0.9(1) Å^2		
Y	0.0293(2)	B_{iso}, S 8g	0.6(1) Å^2		
U	-0.045(1)	Occ, Cu 2c	0.88(2)		
V	0.014(6)	Occ, Sn 2b	0.92(1)		

Figure S13: Rietveld refinement of synchrotron data obtained for annealed sample E.

PDF results

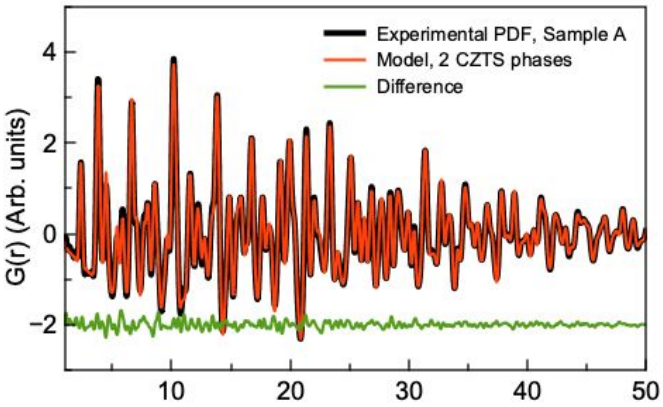


Figure S14: Fit of the PDF obtained for annealed sample A, using two CZTS phases of different domain sizes.

PDF refinement, sample A			
R_W	9.71%	x_S	0.76
a (Å)	5.428	y_S	0.75
c (Å)	10.808	z_S	0.87
delta2	3.9 Å	B_{iso} (Å^2), Cu 2a	0.48
		B_{iso} (Å^2), Cu 2c	0.35
		B_{iso} (Å^2), Zn 2d	0.48
Weight percent, bulk phase	83%	B_{iso} (Å^2), Sn 2b	0.25
Weight percent, nanophase	17%	B_{iso} (Å^2), S 8g	0.17
Average crystallite size, nanophase*	17 Å		

*The structural parameters for the bulk and nanosized phases were constrained to take the same value, and only the scale factors and the size for the nanophase were refined independently. The occupancies for the metals were kept fixed at the values obtained in the corresponding Rietveld refinements.

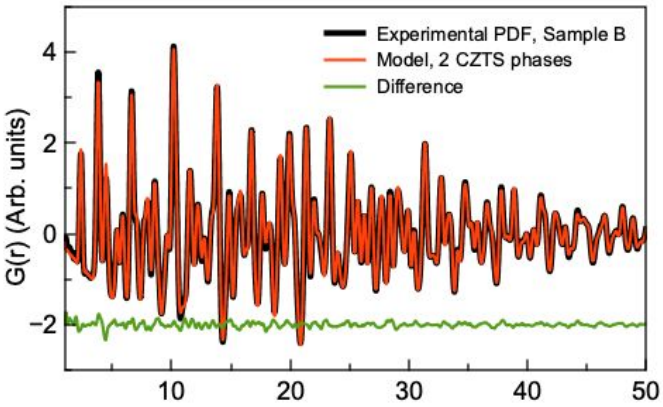


Figure S15: Fit of the PDF obtained for annealed sample B, using two CZTS phases of different domain sizes.

PDF refinement, sample B			
R_W	5.7%	x_S	0.77
a (Å)	5.429	y_S	0.75
c (Å)	10.807	z_S	0.87
delta2	4.18 Å	B_{iso} (Å^2), Cu 2a	0.51
		B_{iso} (Å^2), Cu 2c	0.34
		B_{iso} (Å^2), Zn 2d	0.37
Weight percent, bulk phase	85%	B_{iso} (Å^2), Sn 2b	0.21
Weight percent, nanophase	15%	B_{iso} (Å^2), S 8g	0.27
Average crystallite size, nanophase*	23 Å		

*The structural parameters for the bulk and nanosized phases were constrained to take the same value, and only the scale factors and the size for the nanophase were refined independently. The occupancies for the metals were kept fixed at the values obtained in the corresponding Rietveld refinements.

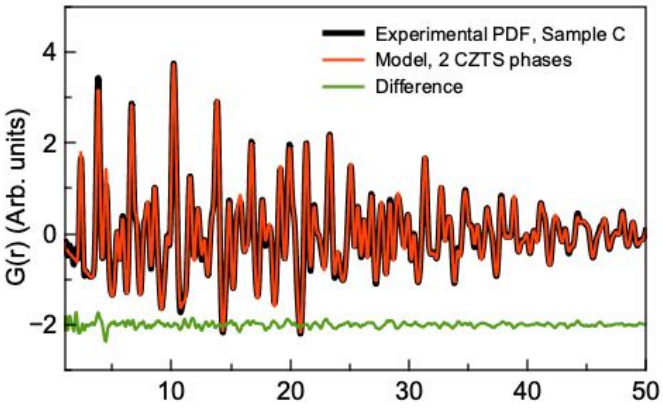


Figure S16: Fit of the PDF obtained for annealed sample C, using two CZTS phases of different domain sizes.

PDF refinement, sample C			
R_W	7.1%	x_S	0.76
a (Å)	5.426	y_S	0.75
c (Å)	10.800	z_S	0.87
delta2	3.99 Å	B_{iso} (Å^2), Cu 2a	0.49
		B_{iso} (Å^2), Cu 2c	0.38
		B_{iso} (Å^2), Zn 2d	0.23
Weight percent, bulk phase	75%	B_{iso} (Å^2), Sn 2b	0.23
Weight percent, nanophase	25%	B_{iso} (Å^2), S 8g	0.25
Average crystallite size, nanophase*	26 Å		

*The structural parameters for the bulk and nanosized phases were constrained to take the same value, and only the scale factors and the size for the nanophase were refined independently. The occupancies for the metals were kept fixed at the values obtained in the corresponding Rietveld refinements.

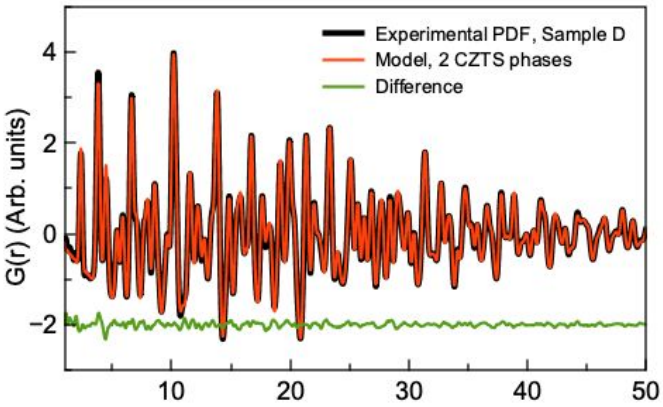


Figure S17: Fit of the PDF obtained for annealed sample D, using two CZTS phases of different domain sizes.

PDF refinement, sample D			
R_W	6.2%	x_S	0.76
a (Å)	5.426	y_S	0.75
c (Å)	10.800	z_S	0.87
delta2	4.10 Å	B_{iso} (Å^2), Cu 2a	0.49
		B_{iso} (Å^2), Cu 2c	0.38
		B_{iso} (Å^2), Zn 2d	0.23
Weight percent, bulk phase	79%	B_{iso} (Å^2), Sn 2b	0.23
Weight percent, nanophase	21%	B_{iso} (Å^2), S 8g	0.25
Average crystallite size, nanophase*	27 Å		

*The structural parameters for the bulk and nanosized phases were constrained to take the same value, and only the scale factors and the size for the nanophase were refined independently. The occupancies for the metals were kept fixed at the values obtained in the corresponding Rietveld refinements.

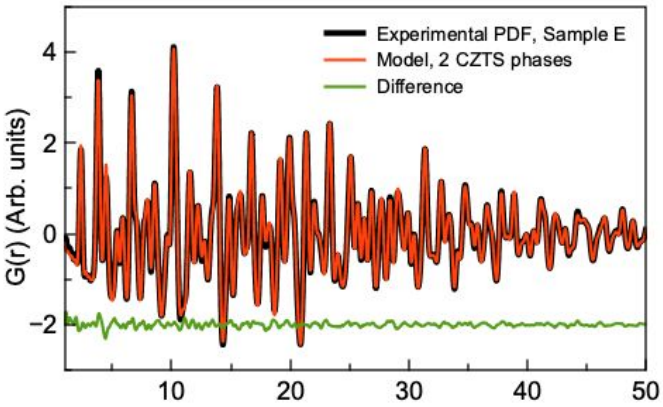


Figure S18: Fit of the PDF obtained for annealed sample E, using two CZTS phases of different domain sizes.

PDF refinement, sample D			
R_W	6.0%	x_S	0.76
a (Å)	5.427	y_S	0.75
c (Å)	10.803	z_S	0.87
delta2	4.33 Å	B_{iso} (Å^2), Cu 2a	0.49
		B_{iso} (Å^2), Cu 2c	0.38
		B_{iso} (Å^2), Zn 2d	0.23
Weight percent, bulk phase	81%	B_{iso} (Å^2), Sn 2b	0.23
Weight percent, nanophase	19%	B_{iso} (Å^2), S 8g	0.25
Average crystallite size, nanophase*	30 Å		

*The structural parameters for the bulk and nanosized phases were constrained to take the same value, and only the scale factors and the size for the nanophase were refined independently. The occupancies for the metals were kept fixed at the values obtained in the corresponding Rietveld refinements.