Electronic Supplementary Information

Observation and enhancement through alkali metal doping of *p*-type conductivity in the layered oxyselenides $Sr_2ZnO_2Cu_2Se_2$ and $Ba_2Zn_{1-x}O_{2-x}Cu_2Se_2$

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Final refinements of $Sr_2ZnO_2Cu_2Se_2$ assuming single site oxygen in *I*4/*mmm*

Atom	X	Y	Z	Occupancy	U_{iso} / Å^2
Cu1	0.5	0	0.25	1	0.0287(7)
Se1	0	0	0.16790(7)	1	0.0213(6)
Sr1	0.5	0.5	0.08771(6)	1	0.0174(6)
Zn1	0	0	0	1	0.0321(11)
O1	0.5	00	0	1	0.029(3)

Table S1. Unit cell parameters for $Sr_2ZnO_2Cu_2Se_2$, refined from room temperature powder XRD in the *I*4/*mmm* space group. The lattice parameters were *a* = 4.06703(4) Å and *c* = 18.38487(19) Å. Fit parameters were found to be wRp = 4.54% and Rf2 = 4.35%, with a sample purity of 95.2%.

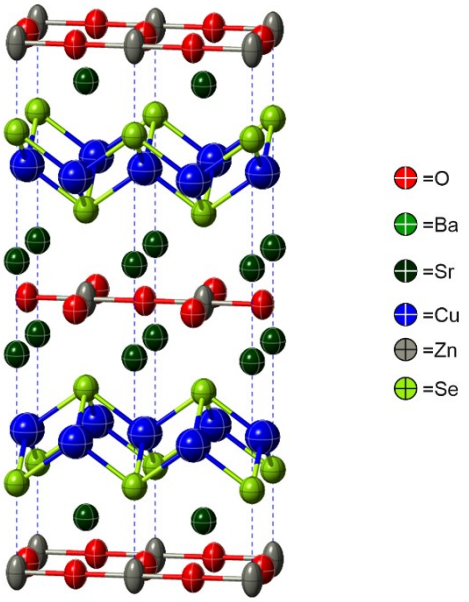

Figure S1. Representation of the unit cell of $Sr_2ZnO_2Cu_2Se_2$ derived from SXRD in the *I*4/*mmm* space group at 100 K, showing the refined anisotropic displacement ellipsoids.

					Displacement parameters / 1000 x Å^2		
Atom	*x*	*y*	*z*	occupancy	U_{11}	U_{22}	U_{33}
Cu1	0.5	0	0.75	1	9.4(3)	9.4(3)	9.0(4)
Se1	0.5	0.5	0.66865(4)	1	4.9(2)	4.9(2)	5.8(3)
Sr1	0	0	0.41193(5)	1	4.9(3)	4.9(3)	5.8(4)
Zn1	0.5	0.5	0.5	1	3.3(3)	3.3(3)	10.2(6)
O1	0.5	0	0.5	1	5(2)	4(2)	7(2)

Table S2. Unit cell parameters for $Sr_2ZnO_2Cu_2Se_2$, refined from single crystal XRD in *I*4/*mmm* space group at 100 K. Lattice parameters found to be *a* = 4.0562(2) Å, *c* = 18.2727(15) Å.

					Displacement parameters / 1000 x Å^2		
Atom	*x*	*y*	*z*	occupancy	U_{11}	U_{22}	U_{33}
Cu1	0	0.5	0.25	1	16.0(3)	16.0(3)	15.6(3)
Se1	0	0	0.16853(2)	1	6.2(3)	6.2(3)	9.8(3)

Sr1	0	0	0.41204(3)	1	6.3(2)	6.3(2)	8.7(1)
Zn1	0	0	0	1	3.5(6)	3.5(6)	21.5(3)
O1	0	0.5	0	1	8.5(5)	9.0(7)	11.1(6)

Table S3. Unit cell parameters for $Sr_2ZnO_2Cu_2Se_2$, refined from Neutron TOF powder diffraction in *I*4/*mmm* space group at 298(2) K. Lattice parameters found to be a = 4.06518(4) Å, c = 18.3751(2) Å

Initial refinements of $Ba_2ZnO_2Cu_2Se_2$ assuming single site oxygen in *I*4/*mmm* – later rejected

Atom	*x*	*y*	*z*	Occupancy	U_{iso} / Å^2
Cu1	0.5	0	0.25	1	0.00276(10
Se1	0	0	0.17555(10)	1	0.0163(9)
Ba1	0.5	0.5	0.09195(7)	1	0.0116(5)
Zn1	0	0	0	0.997(9)	0.0300(20)
O1	0.5	0	0	1	0.0690(60)

Table S4. Unit cell parameters for $Ba_2ZnO_2Cu_2Se_2$, refined from RT powder XRD in the *I*4/*mmm* space group. The lattice parameters were a = 4.20905(4) Å and c= 19.03416(19) Å. Fit parameters were found to be Rw_p = 3.863% and R_f^2 = 4.664%, with a sample purity of 96.8%. This provides a reasonable fit to the data – but later analysis indicates that the oxygen site is split leading to a disordered linear zinc environment.

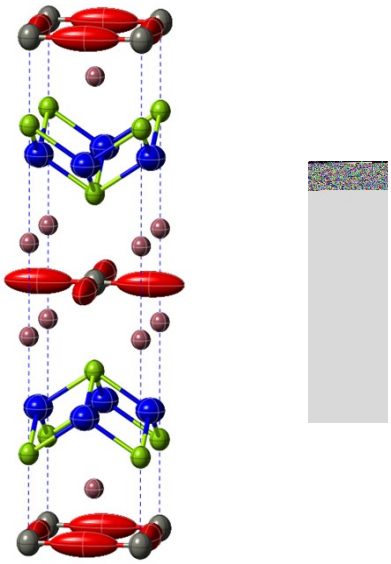

Figure S2. Representation of the unit cell of $Ba_2ZnO_2Cu_2Se_2$ derived from SXRD in the *I*4/*mmm* space group at 100 K, showing the refined elongated anisotropic displacement ellipsoids which indicate the structural distortion.

				Occupancy	Displacement parameters / 1000 x Å^2		
Atom	*x*	*y*	*z*		U_{11}	U_{22}	U_{33}
Cu1	0.5	0	0.25	1	7.87(19)	7.87(19)	6.1(3)
Se1	0.5	0.5	0.32467(2)	1	3.54(15)	3.54(15)	4.6(2)
Ba1	0	0	0.40746(2)	1	3.25(12)	3.25(12)	3.64(16)
Zn1	0.5	0.5	0.5	0.987(4)	4.9(3)	4.9(3)	6.7(4)
O1	0.5	0	0.5	1	45(2)	4.6(15)	6.1(16)

Table S5. Unit cell parameters for $Ba_2ZnO_2Cu_2Se_2$, refined from SXRD in *I*4/*mmm* space group at 100 K. Lattice parameters found to be *a* = 4.1871(2) Å, *c* = 18.9579(12) Å. Note very large U_{11} parameter.

				Occupancy	Displacement parameters / 1000 x Å^2		
Atom	*x*	*y*	*z*		U_{11}	U_{22}	U_{33}
Cu1	0	0.5	0.25	1	21.1(4)	21.1(4)	13.7(4)
Se1	0	0	0.17545(3)	1	8.04(7)	8.04(7)	10.8(5)

Ba1	0.5	0.5	0.40773(6)	1	7.3(1)	7.3(1)	4.6(8)
Zn1	0	0	0	0.931(3)	9.1(5)	9.1(5)	19.5(9)
O1	0.5	0	0	0.980(2)	7.3(5)	55.9(9)	12.1(3)

Table S6. Unit cell parameters for $Ba_2ZnO_2Cu_2Se_2$, refined from NPD in *I*4/*mmm* space group at 298 (2)K . Lattice parameters found to be a = 4.20572(5) Å, c = 19.0203(3) Å. Rw_p = 4.12%. Note very large U_{22} parameter.

				Occupancy	Displacement parameters / 1000 x Å^2		
Atom	*x*	*y*	*z*		U_{11}	U_{22}	U_{33}
Cu1	0	0.5	0.25	1	3.8(3)	3.8(3)	2.4(3)
Se1	0	0	0.17528(3)	1	2.2(3)	2.2(3)	2.6(4)
Ba1	0.5	0.5	0.40735(5)	1	1.3(3)	1.3(3)	0.0 (5)
Zn1	0	0	0	0.955(3)	1.6(5)	1.6(5)	3.8(7)
O1	0.5	0	0	0.987(3)	5.7(6)	41.6(10)	7.2(6)

Table S7. Unit cell parameters for $Ba_2ZnO_2Cu_2Se_2$, refined from NPD in *I*4/*mmm* space group at low temperature, 2 K. Lattice parameters found to be a = 4.18634(9) Å, c = 18.9683(4) Å. Rw_p = 1.91%. Note very large U_{22} parameter.

Comparison of the fit parameters for the three competing structural models for $Ba_2ZnO_2Cu_2Se_2$

As discussed in the main paper, the extended oxygen ellipsoid was indicative of a shift from square planar to linear zinc geometry. The electron diffraction data rules out both the conventional tetragonal structure and the ordered orthorhombic distortion, indicating the split site tetragonal model as the most reasonable. For completeness all three models were used with the neutron diffraction data, which confirmed that the split site also gave better or equivalent fits to the data.

Experimental temperature	Split *I*4/*mmm*	Unsplit *I*4/*mmm*	*Cmca*
2 K	1.89%	1.91%	1.88%
RT	4.06%	4.12%	4.08%

Table S8. Comparison of Rw_p fit values for the three competing models.

Final refinements of $Ba_2ZnO_2Cu_2Se_2$ modelled with split site oxygen in *I*4/*mmm*

				Occupancy	Displacement parameters / 1000 x Å^2		
Atom	*x*	*y*	*z*		U_{11}	U_{22}	U_{33}
Cu1	0.5	0	0.25	1	7.81(19)	7.81(19)	6.0(3)
Se1	0.5	0.5	0.32466(2)	1	3.48(15)	3.48(15)	4.6(2)
Ba1	0	0	0.40746(2)	1	3.41(12)	3.41(12)	3.78(16)
Zn1	0.5	0.5	0.5	0.991(4)	5.1(3)	5.1(3)	6.7(4)
O1	0.0435(11)	0.5	0.5	0.4972	5.5(8)	5.5(8)*	5.5(8)*

Table S10. Unit cell parameters for $Ba_2ZnO_2Cu_2Se_2$, refined from SXRD in *I*4/*mmm* space group at 100 K. Lattice parameters found to be *a* = 4.1871(2) Å, *c* = 18.9579(12) Å. R_1 = 1.29%, Rw2 = 2.78%, Gof = 1.104, Largest diff. peak/hole / e Å-3 0.64/-0.95.

				Occupancy	Displacement parameters / 1000 x Å^2		
Atom	*x*	*y*	*z*		U_{11}	U_{22}	U_{33}
Cu1	0	0.5	0.25	1	3.7(2)	3.7(2)	3.9(3)
Se1	0	0	0.17523(3)	1	2.6(2)	2.6(2)	4.3(3)
Ba1	0.5	0.5	0.40735(5)	1	1.4(2)	1.4(2)	1.5(4)
Zn1	0	0	0	0.958(3)	3.4(4)	3.4(4)	4.6(7)
O1	0	0.5433(4)	0	0.4874(16) / 0.5	3.9(60	1.3(6)	7.5(6)

Table S11. Unit cell parameters for $Ba_2ZnO_2Cu_2Se_2$, refined from NPD in *I*4/*mmm* space group at low temperature, 2 K. Lattice parameters found to be *a* = 4.18641(9) Å, *c* = 18.9687(4) Å. Rw_p = 1.89%

				Occupancy	Displacement parameters / 1000 x Å^2		
Atom	*x*	*y*	*z*		U_{11}	U_{22}	U_{33}
Cu1	0	0.5	0.25	1	20.2(4)	20.2(4)	14.9(5)
Se1	0	0	0.17543(3)	1	8.2(3)	8.2(3)	11.2(4)
Ba1	0	0	0.40777(5)	1	7.1(4)	7.1(4)	5.0(5)
Zn1	0	0	0	0.940(3)	9.6(6)	9.6(6)	20.7(9)
O1	0	0.5492(4)	0	0 0.4853(14) / 0.5	5.3(6)	5.3(6)	12.4(6)

Table S12. Unit cell parameters for $Ba_2ZnO_2Cu_2Se_2$, refined from NPD in *I*4/*mmm* space group at room temperature, 298 K. Lattice parameters found to be *a* = 4.20579(9) Å, *c* = 19.0207(4) Å. Rw_p = 4.06%

X-ray diffraction data and Rietveld refinement fits of doped samples of $A_xBa_{2-x}ZnO_2Cu_2Se_2$, A = Na or K

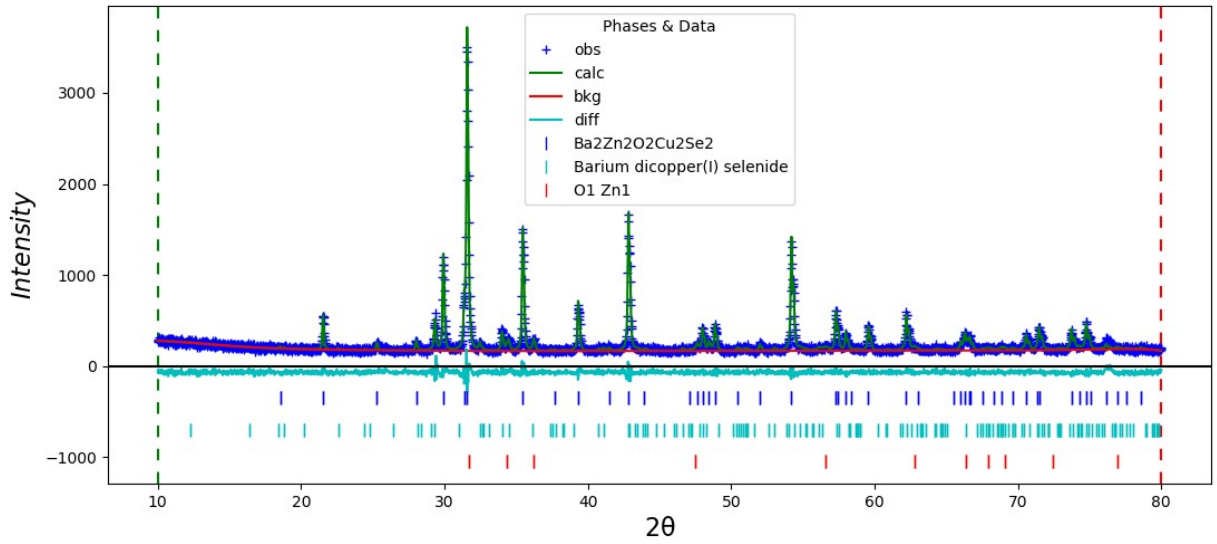

Figure S3. Rietveld refinement of attempted synthesis of $Na_{0.05}Ba_{1.95}ZnO_2Cu_2Se_2$. Sample purity of 85.5% with wRp of 6.1%.

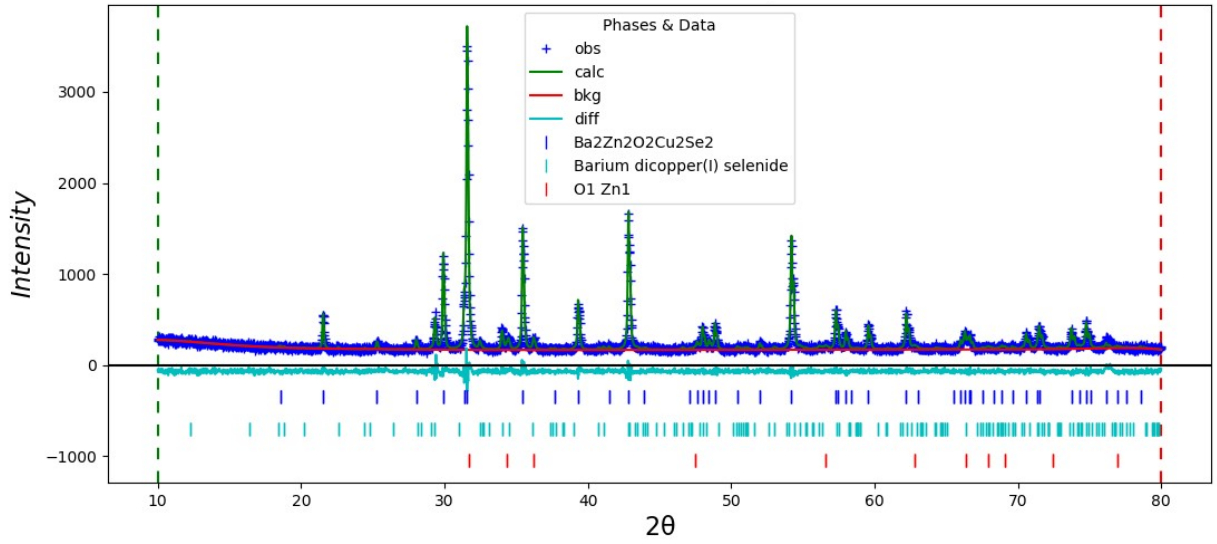

Figure S4. Rietveld refinement of attempted synthesis of $Na_{0.1}Ba_{1.9}ZnO_2Cu_2Se_2$. Sample purity of 83.7% with wRp of 7.6%.

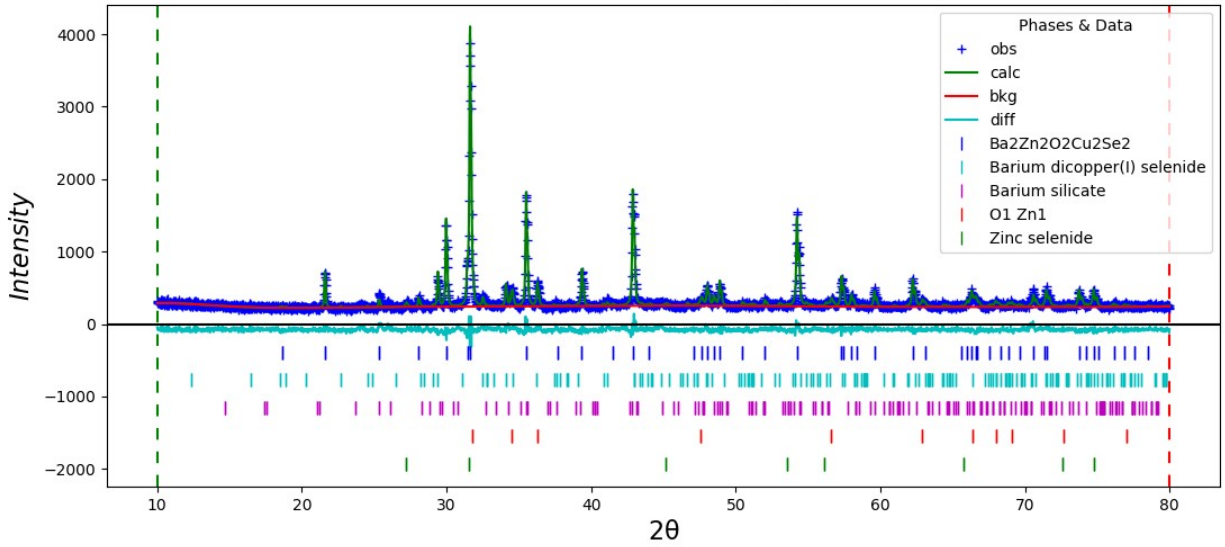

Figure S5. Rietveld refinement of attempted synthesis of $Na_{0.33}Ba_{1.67}ZnO_2Cu_2Se_2$. Sample purity of 78.2% with wRp of 7.4%

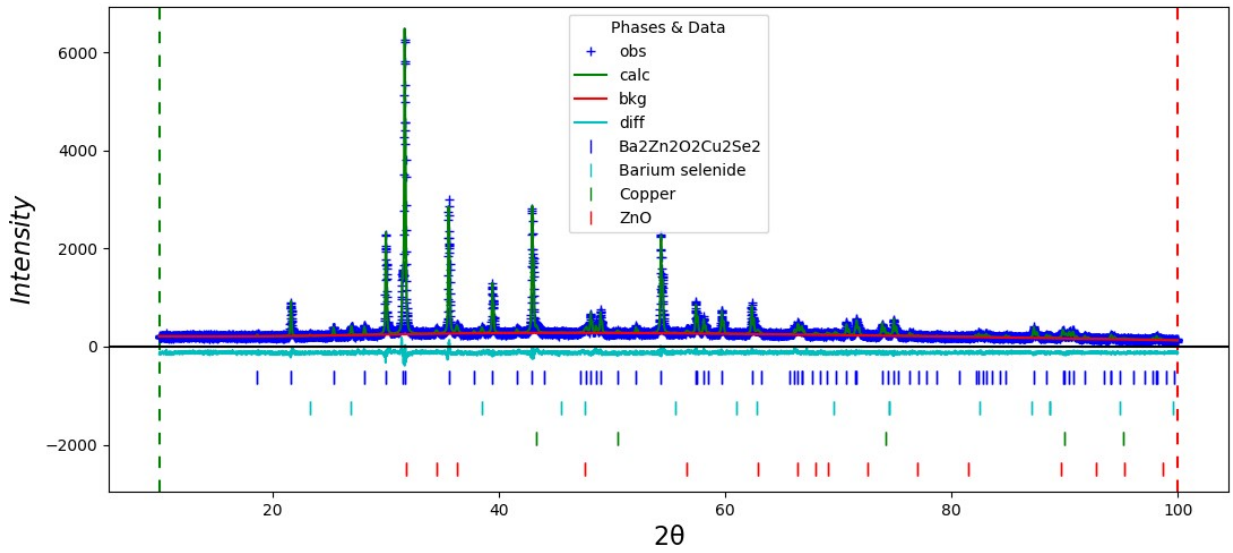

Figure S6. Rietveld refinement of attempted synthesis of $K_{0.05}Ba_{1.95}ZnO_2Cu_2Se_2$. Sample purity of 93.0% with wRp of 6.9%.

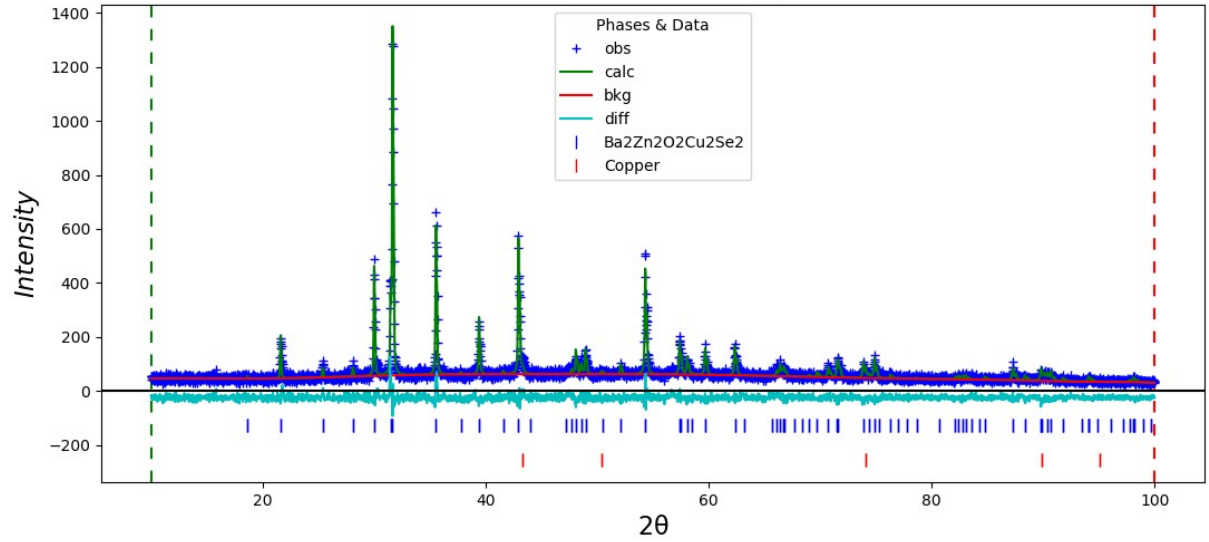

Figure S7. Rietveld refinement of attempted synthesis of $K_{0.1}Ba_{1.9}ZnO_2Cu_2Se_2$. Sample purity of 98.2% with wRp of 13.7%.

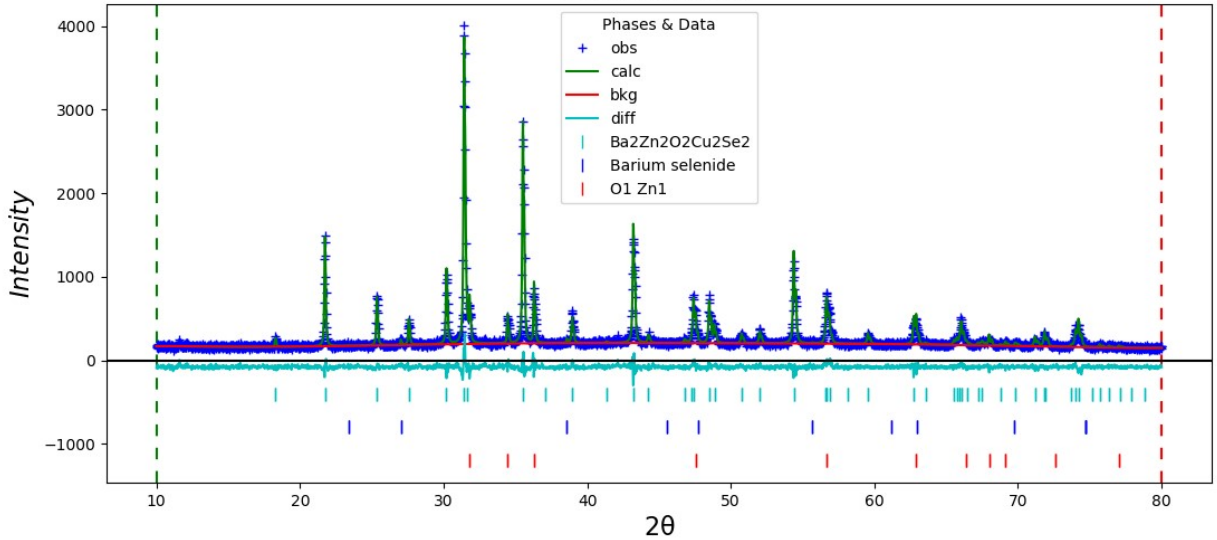

Figure S8. Rietveld refinement of attempted synthesis of $K_{0.33}Ba_{1.67}ZnO_2Cu_2Se_2$. Sample purity of 75.4% with wRp of 7.6%.

X-ray diffraction data and Rietveld refinement fits of doped samples of $A_xBa_{2-x}ZnO_2Cu_2Se_2$, A = Na or K

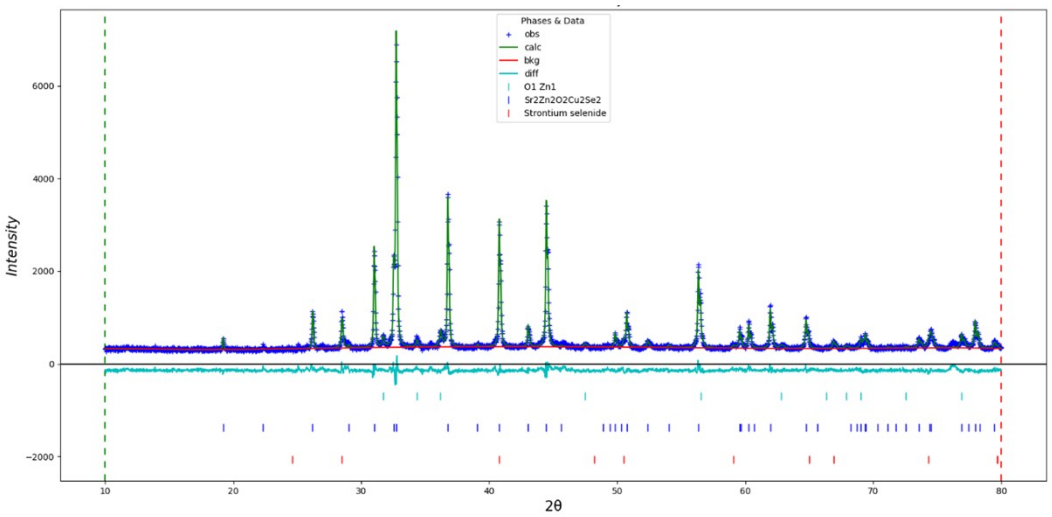

Figure S9. Rietveld refinement of attempted synthesis of $Na_{0.05}Sr_{1.95}ZnO_2Cu_2Se_2$. Sample purity of 90.9% with wRp of 6.6%.

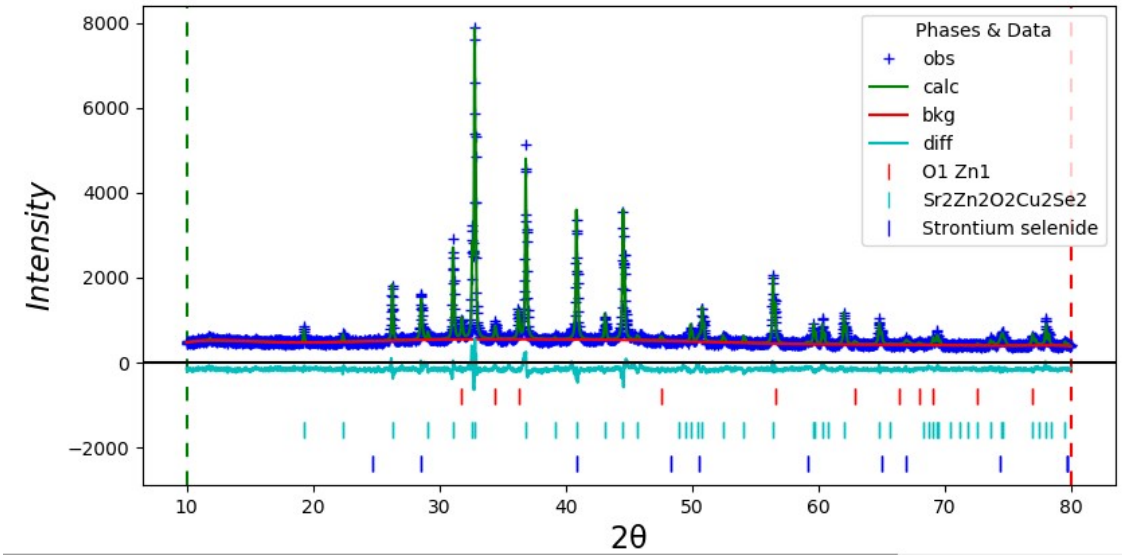

Figure S10. Rietveld refinement of attempted synthesis of $Na_{0.1}Sr_{1.9}ZnO_2Cu_2Se_2$. Sample purity of 84.4% with wRp of 7.1%.

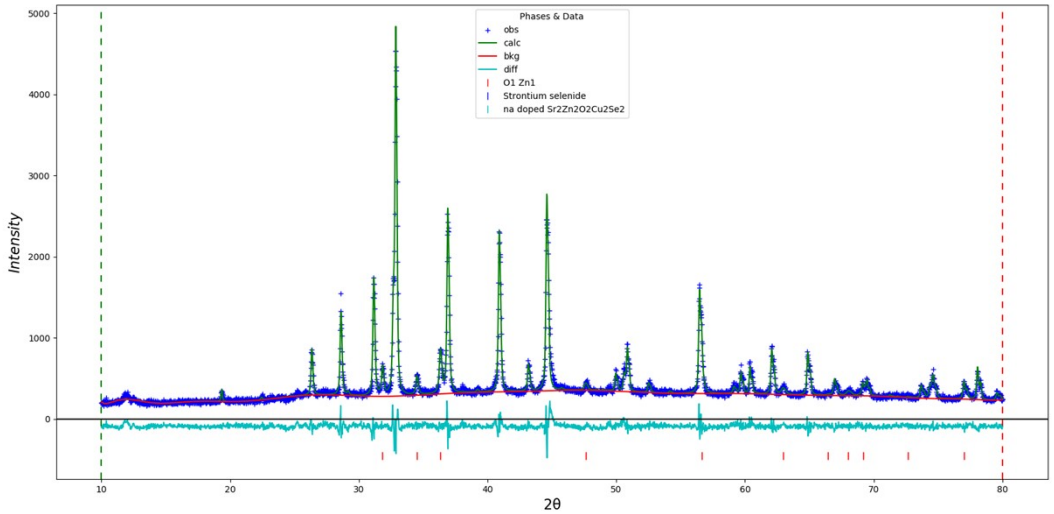

Figure S11. Rietveld refinement of attempted synthesis of $Na_{0.33}Sr_{1.67}ZnO_2Cu_2Se_2$. Sample purity of 81.5% with wRp of 7.7%.

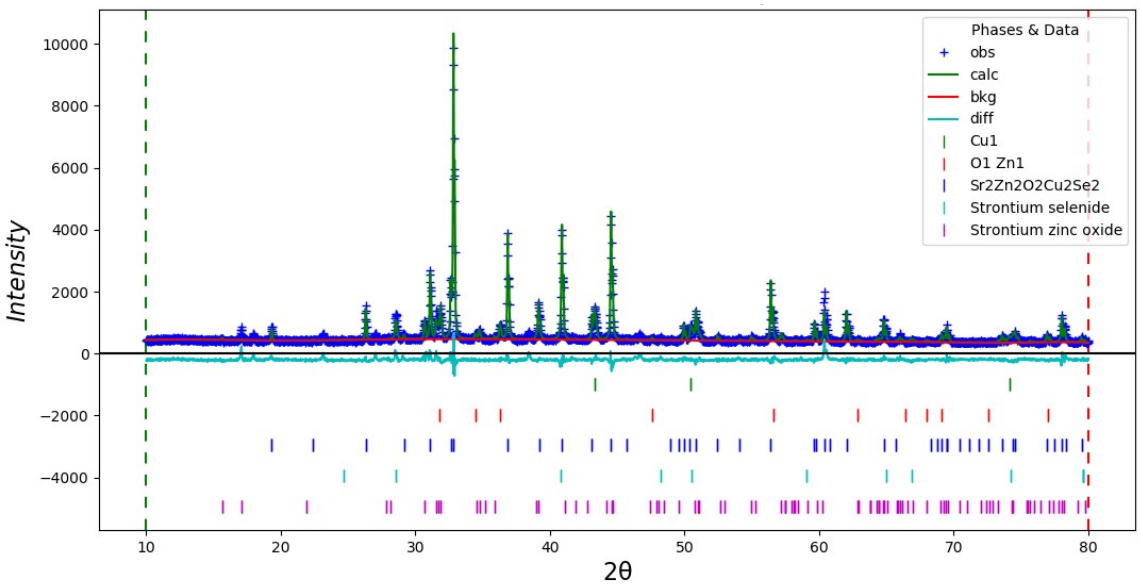

Figure S12. Rietveld refinement of attempted synthesis of $K_{0.05}Sr_{1.95}ZnO_2Cu_2Se_2$. Sample purity of 70% with wRp of 8.2%.

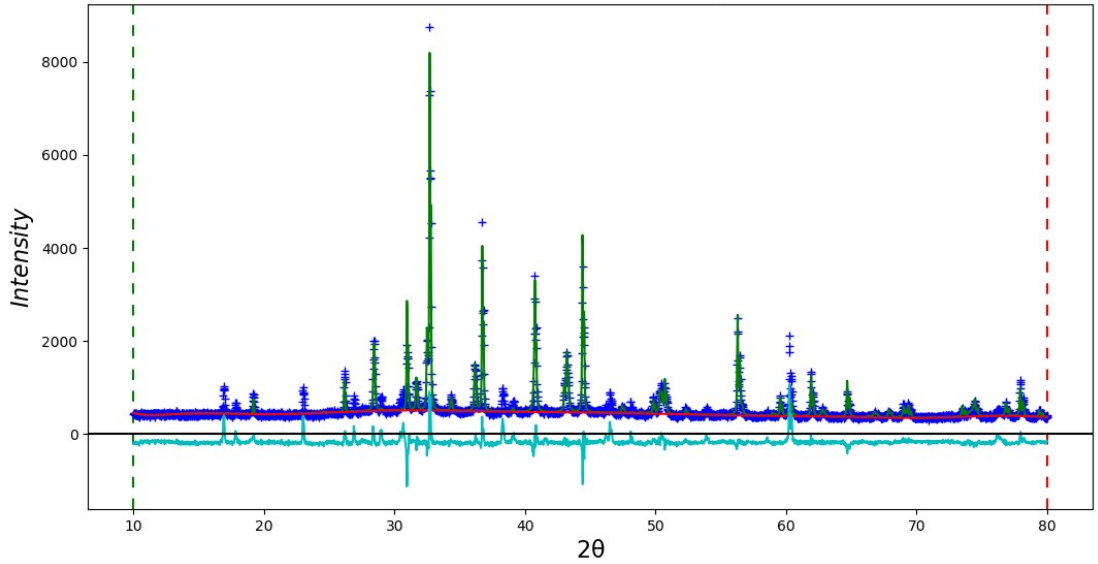

Figure S13. Rietveld refinement of attempted synthesis of $K_{0.1}Sr_{1.95}ZnO_2Cu_2Se_2$. Sample purity of 66% with wRp of 11.5%.

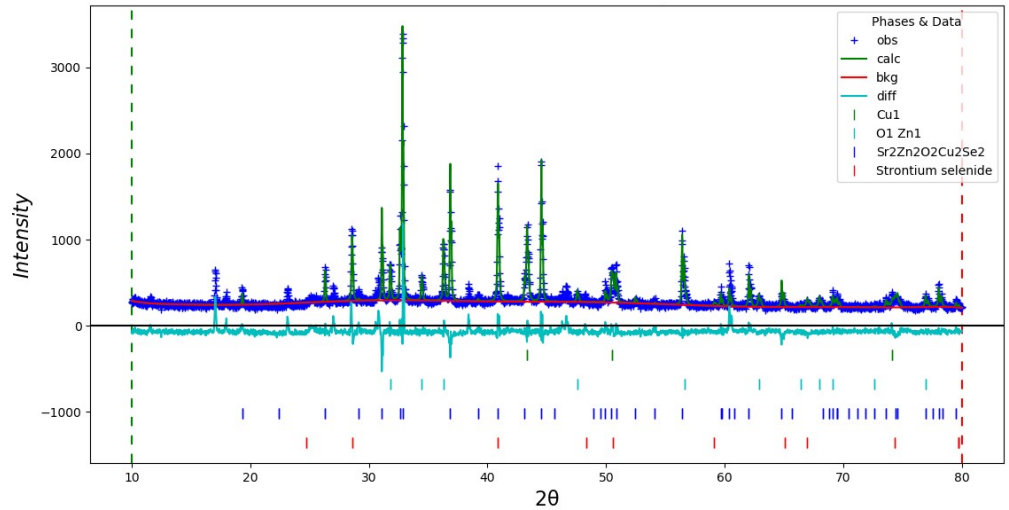

Figure S13. Rietveld refinement of attempted synthesis of $K_{0.1}Sr_{1.95}ZnO_2Cu_2Se_2$. Sample purity of 64.8% with wRp of 10.6%.

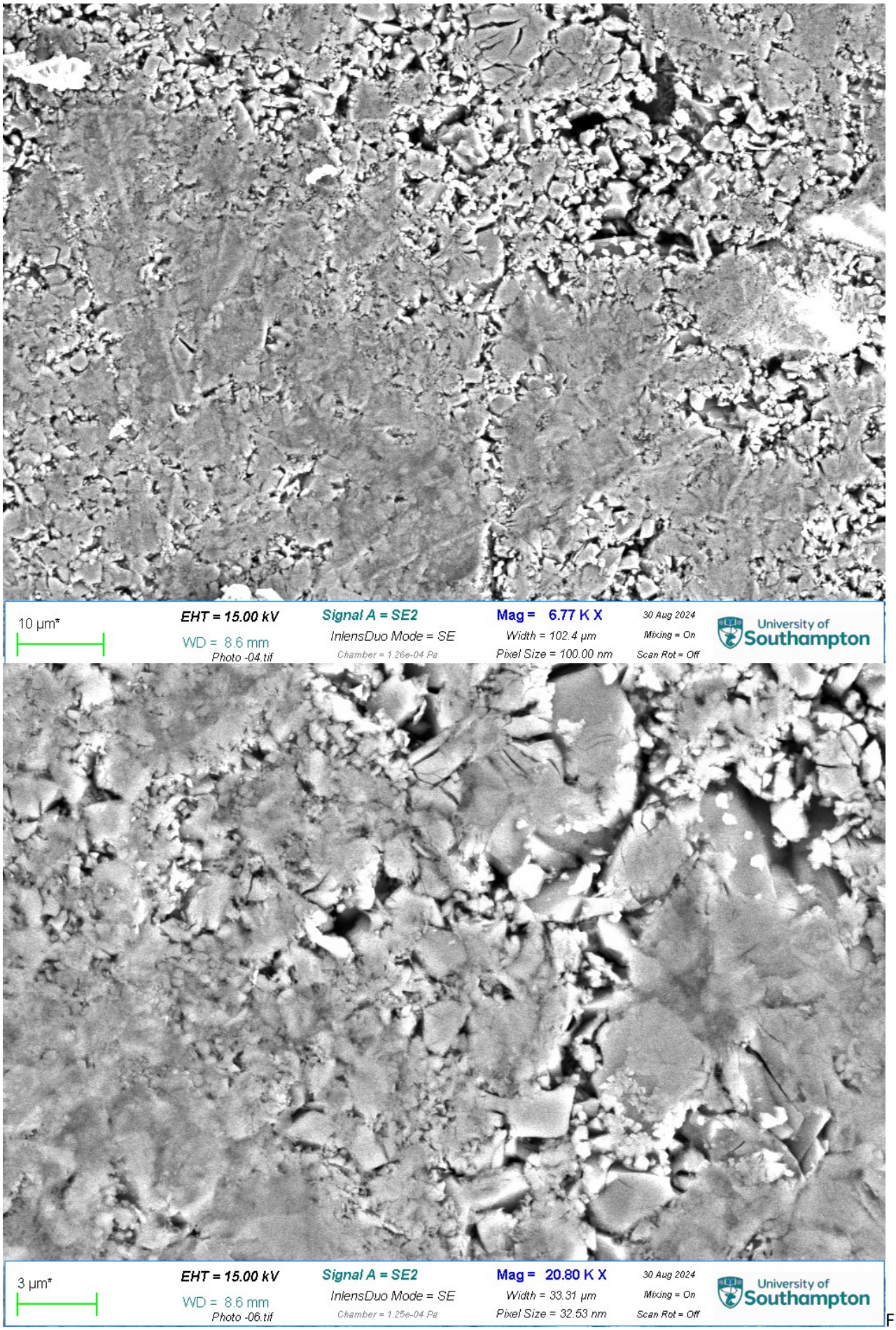

Figure S14. SEM images taken from the pellet surface of $K_{0.1}Ba_{1.9}ZnO_2Cu_2Se_2$

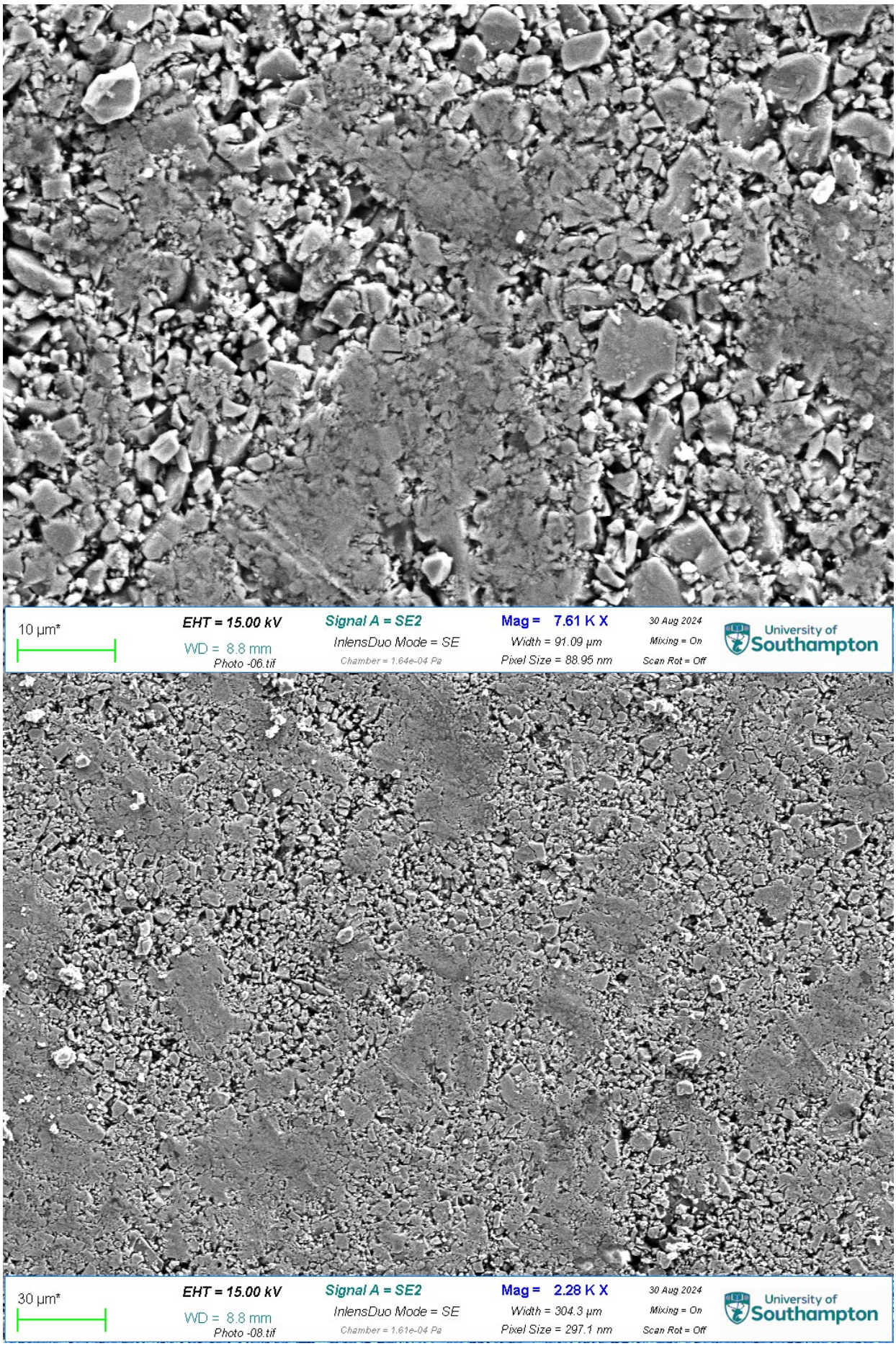

Figure S15. SEM images taken from the pellet surface of $Na_{0.1}Sr_{1.9}ZnO_2Cu_2Se_2$