

Supplementary Information for:

Oxide Ion Dynamics and Structure-Property Relationships in $A_3\text{OhTd}_2\text{O}_{7.5}$ Ionic Conductors (A = Ba, Sr; Oh = Y; Td = Ga, Zn)

Oliver J. Wagstaff[†], Maxim Avdeev^{‡, §}, Stewart J. Clark^{||}, John S. O. Evans^{†,*}, Ivana Radosavljevic Evans^{†,*}

[†]*Department of Chemistry, Durham University, Lower Mount Joy, South Road, Durham DH1 3LE, United Kingdom*

[‡]*Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, Menai 2234, Australia*

[§]*School of Chemistry, The University of Sydney, Sydney NSW 2006, Australia*

^{||}*Department of Physics, Durham University, Lower Mount Joy, South Road, Durham DH1 3LE, United Kingdom*

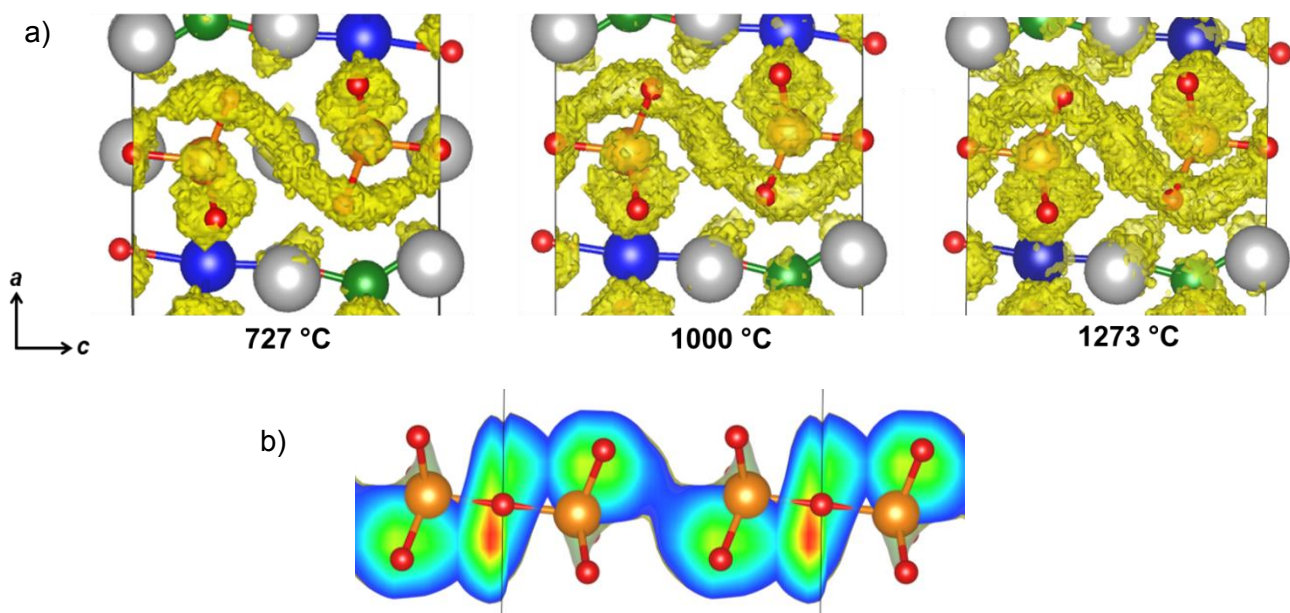


Figure S1. a) Cloud plots showing volume visited by oxide ions at three simulation temperatures. b) Probability density distribution of oxide ions at 1000 °C along the sinusoidal diffusion pathway where the blue-to-red heat map indicates increasing probability.

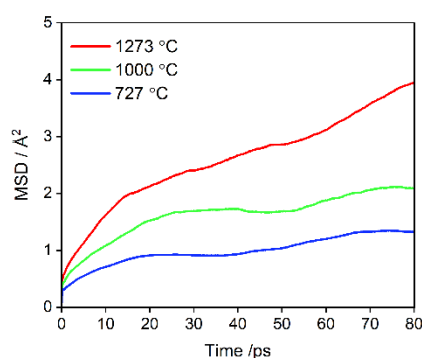


Figure S2. Mean square displacements for all oxygen atoms in the simulations at 727, 1000 and 1273 °C.

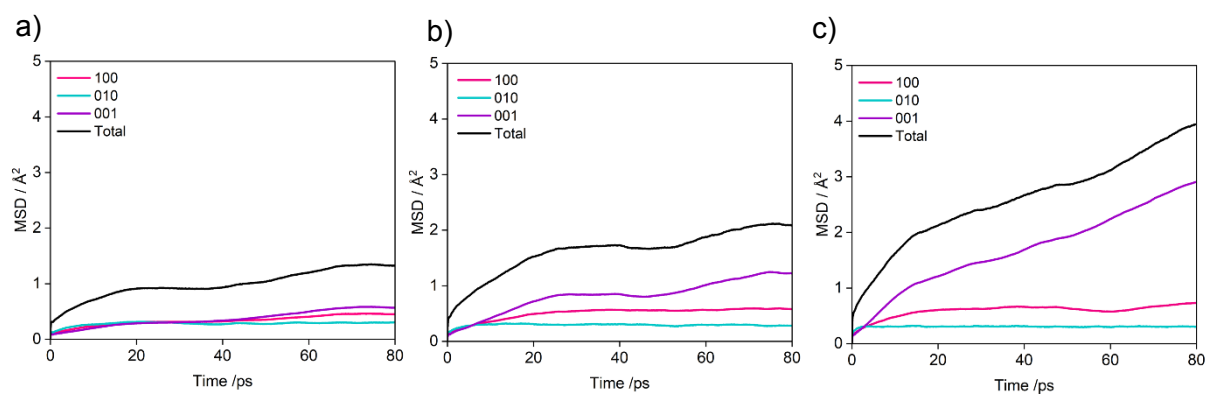


Figure S3. Mean square displacement components along the *a*(100), *b*(010), *c*(001) axes for all oxygen atoms in the simulations at a) 727, b) 1000 and c) 1273 °C.

727 °C

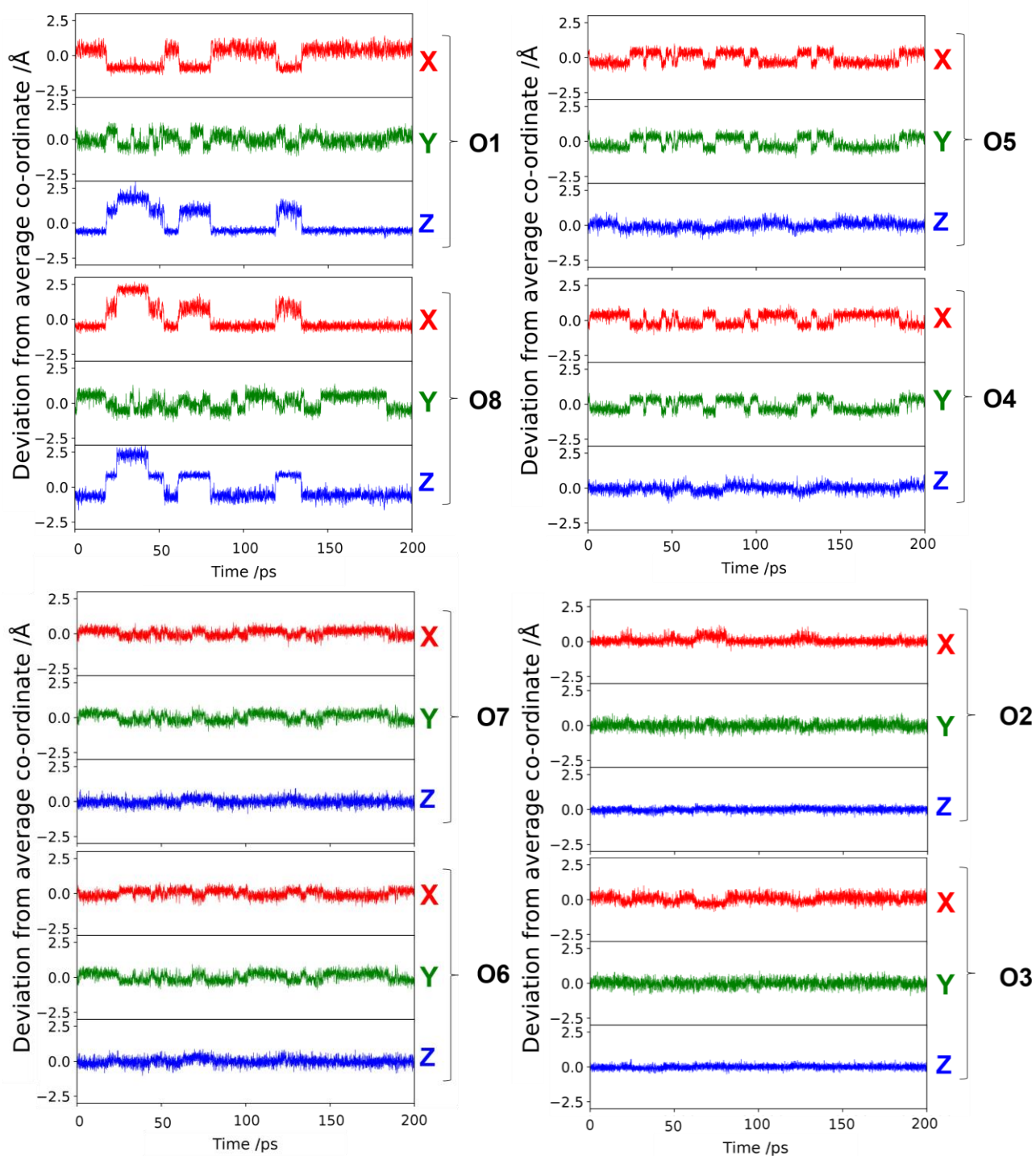


Figure S4. Time evolution of all oxygen positions in the 727 °C simulation.

1000 °C

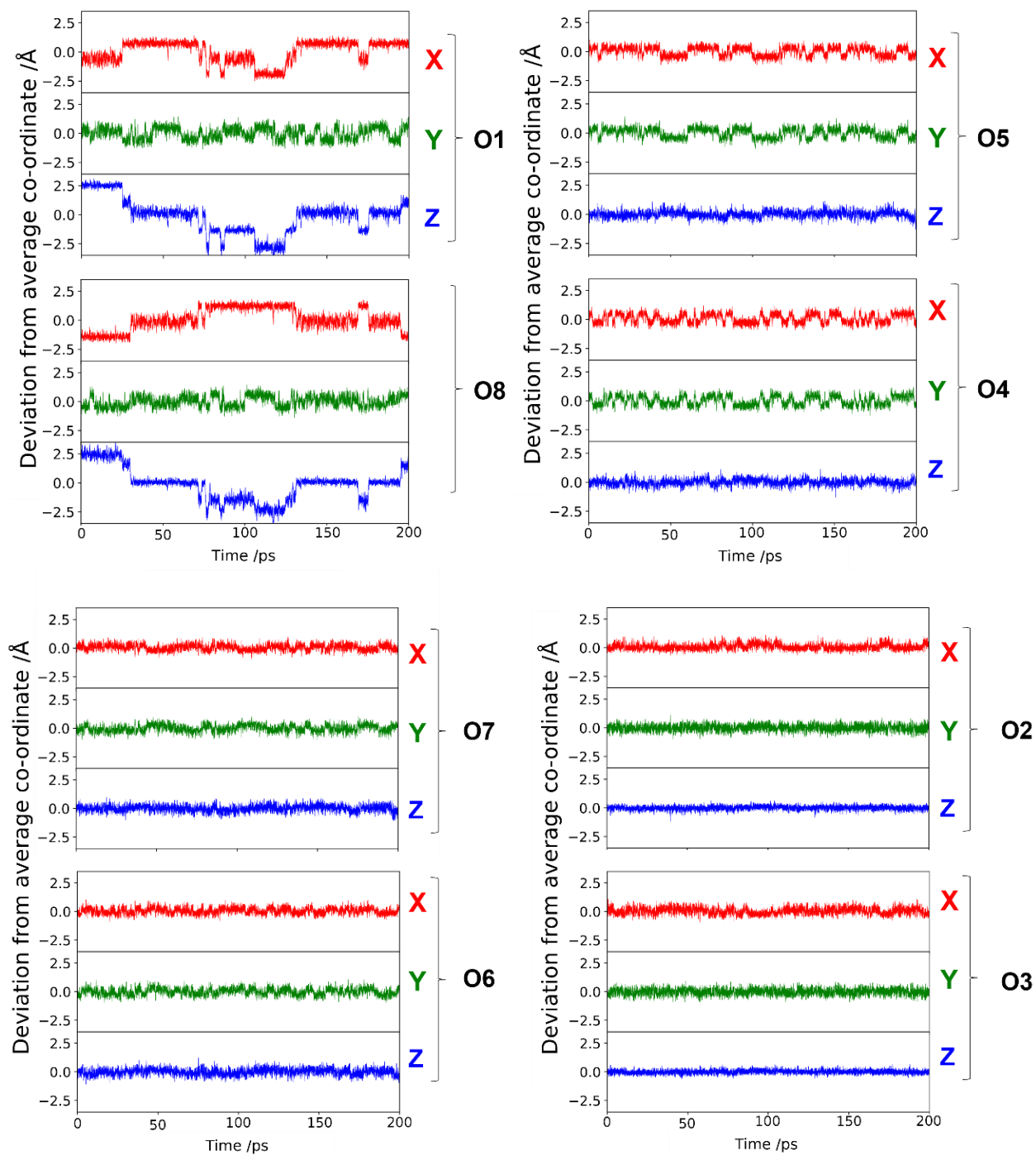


Figure S5. Time evolution of all oxygen positions in the 1000 °C simulation.

1273°C

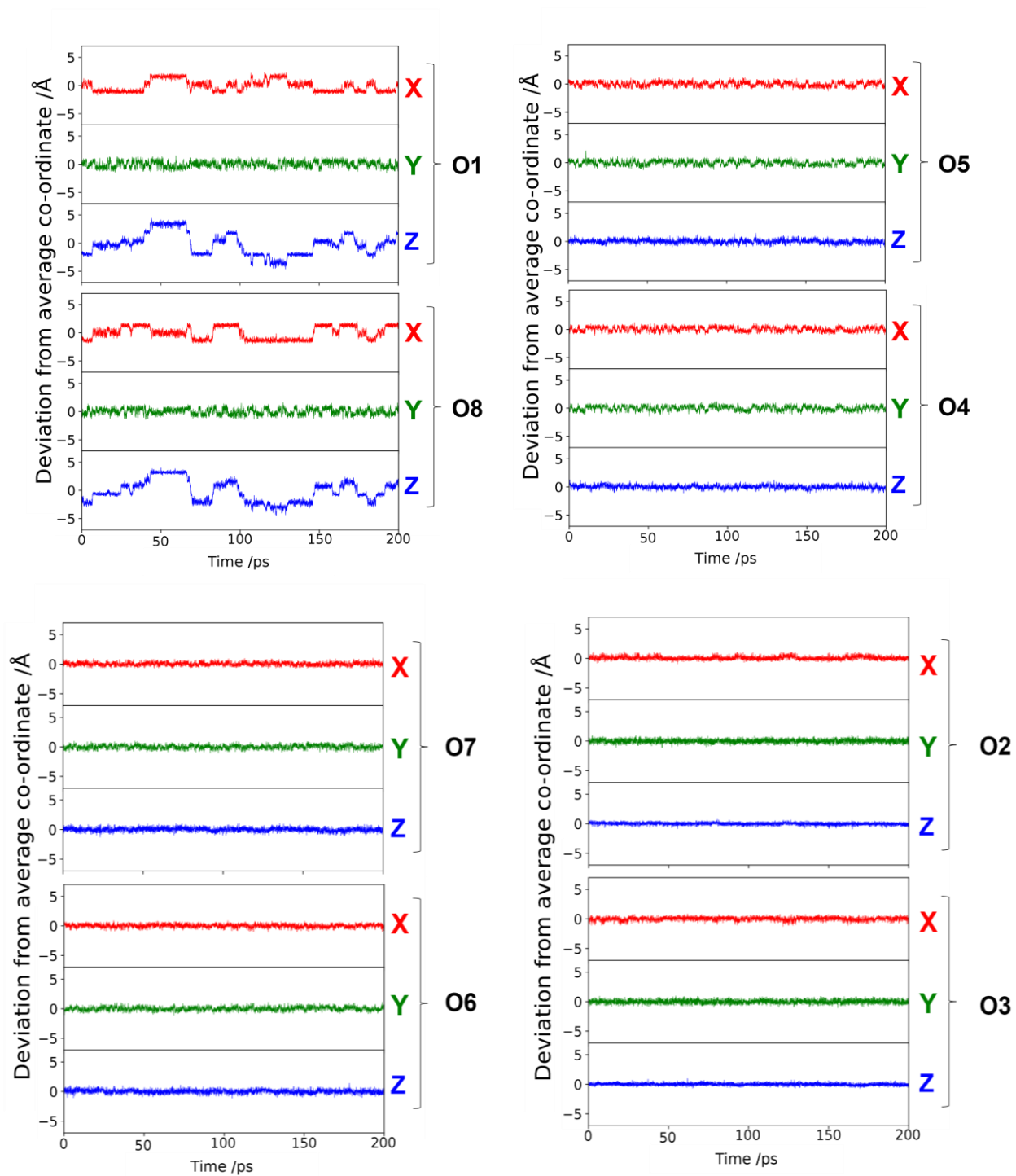


Figure S6. Time evolution of all oxygen positions in the 1273 °C simulation.

Table S1. Synthetic and densification procedures for $\text{Sr}_3\text{YGa}_{2-x}\text{Zn}_x\text{O}_{7.5-x/2}$ and $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{2-x}\text{Zn}_x\text{O}_{7.5-x/2}$ and atmospheres used during impedance spectroscopy measurements.

Compound	Sintering Conditions / time / h @ $T / ^\circ\text{C}$	$\rho_{\text{rel}} / \%$	Atmospheres		
			Air	Dry N_2	Wet N_2
$\text{Sr}_3\text{YGa}_2\text{O}_{7.5}$	92 @ 1200 + 30 @ 1300	91	✓		
$\text{Sr}_3\text{YGa}_{1.95}\text{Zn}_{0.05}\text{O}_{7.475}$	30 @ 1200 + 8 @ 1300	81	✓	✓	✓
$\text{Sr}_3\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$	45 @ 1200 + 10 @ 1300	80	✓	✓	✓
$\text{Sr}_3\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$	40 @ 1200 + 24 @ 1205	87	✓	✓	✓
$\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_2\text{O}_{7.5}$	48 @ 1200	-			
$\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.95}\text{Zn}_{0.05}\text{O}_{7.475}$	60 @ 1200 + 12 @ 1230	86	✓		
$\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$	48 @ 1200 + 15 @ 1250	83	✓	✓	✓
$\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$	68 @ 1200	82	✓		

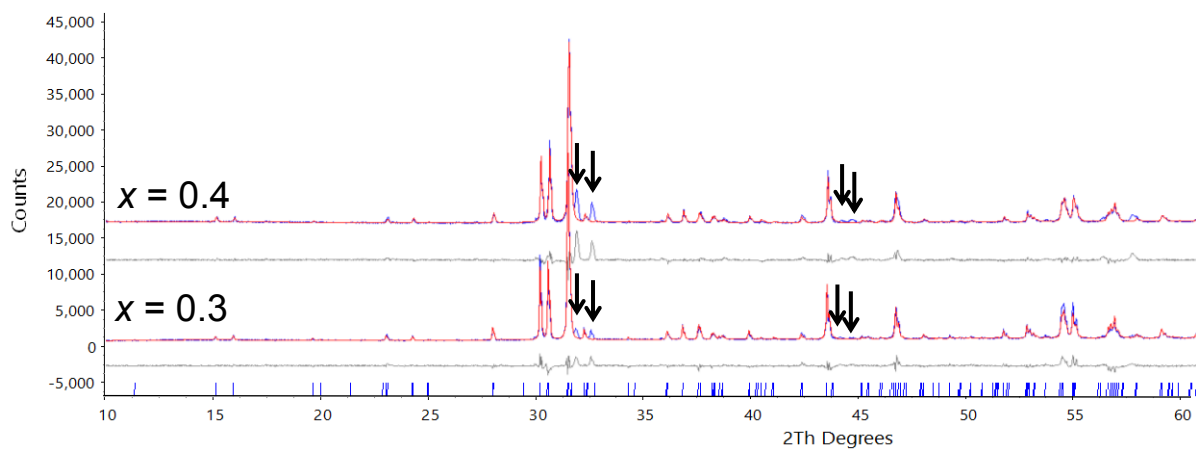


Figure S7. Rietveld fits to $\text{Sr}_3\text{YGa}_{2-x}\text{Zn}_x\text{O}_{7.5-x/2}$ ($x = 0.3, 0.4$) in space group $C2$. Peaks associated with Zn-containing impurities are indicated with black arrows.

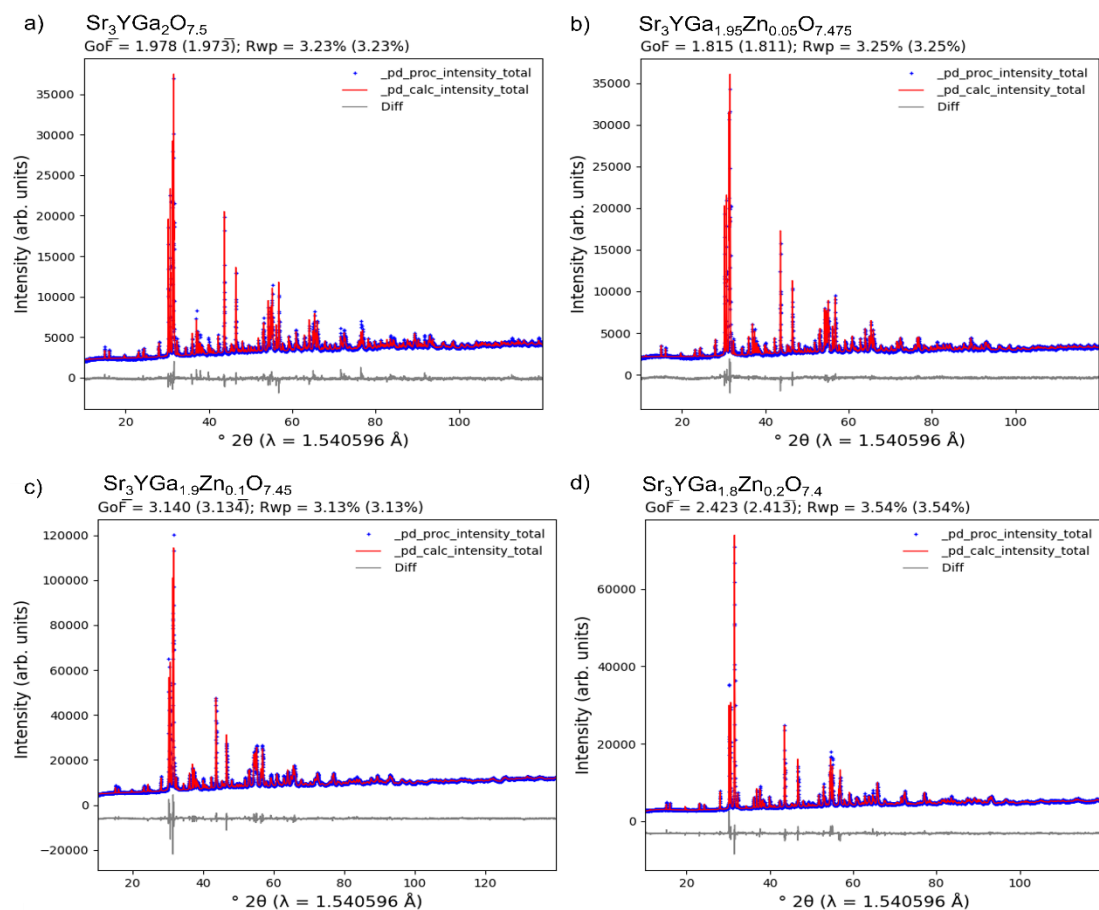


Figure S8. Final Rietveld fits to PXRD data of $\text{Sr}_3\text{YGa}_{2-x}\text{Zn}_x\text{O}_{7.5-x/2}$ compounds a) $x = 0$ b) $x = 0.05$ c) $x = 0.1$ d) $x = 0.2$ in space group $C2$.

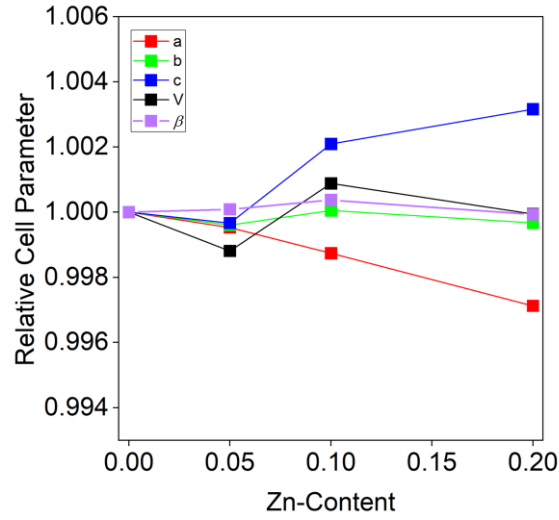


Figure S9. Unit-cell parameter evolution with Zn-content for the $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{2-x}\text{Zn}_x\text{O}_{7.5-x/2}$ series.

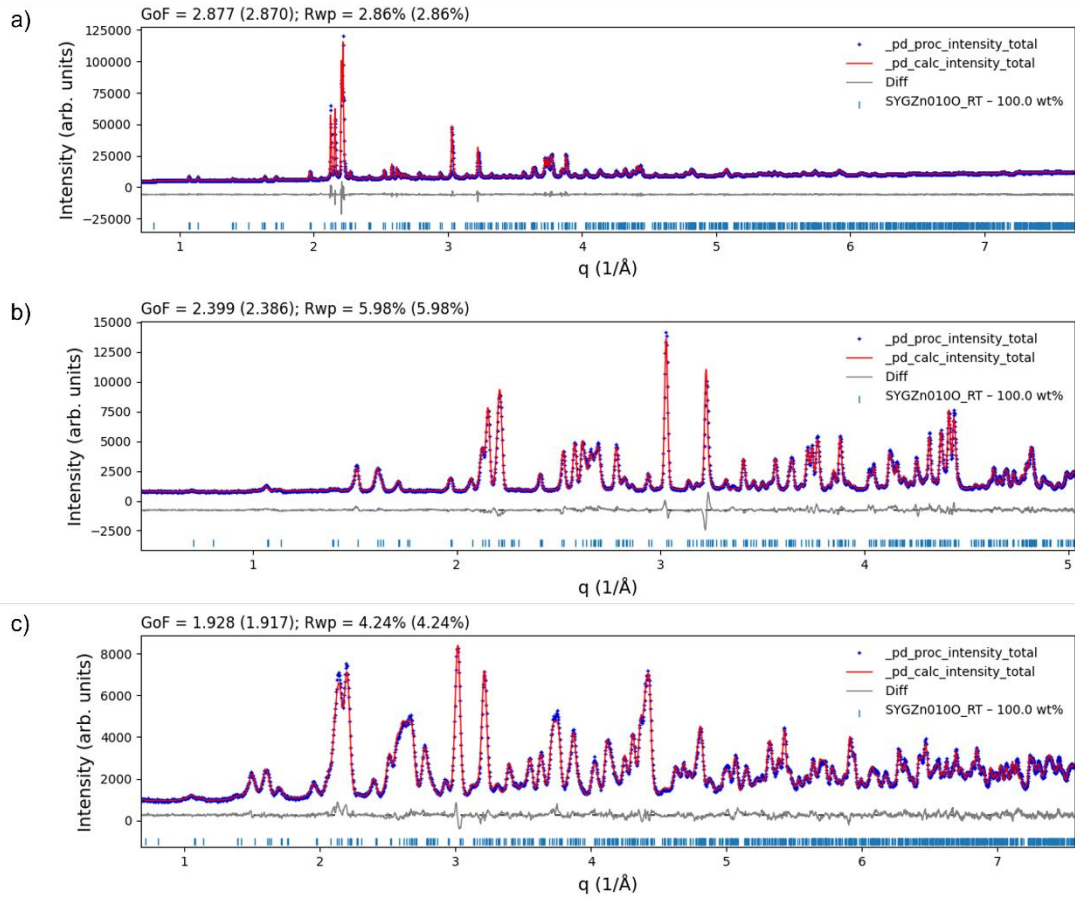


Figure S10. Combined X-ray and neutron Rietveld refinement of $\text{Sr}_3\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$. Measured on a) a laboratory (Cu K α) diffractometer b) ECHIDNA with $\lambda = 2.4395 \text{ \AA}$ and c) $\lambda = 1.622$. Overall $R_{\text{wp}} = 3.25\%$, GOF = 2.57.

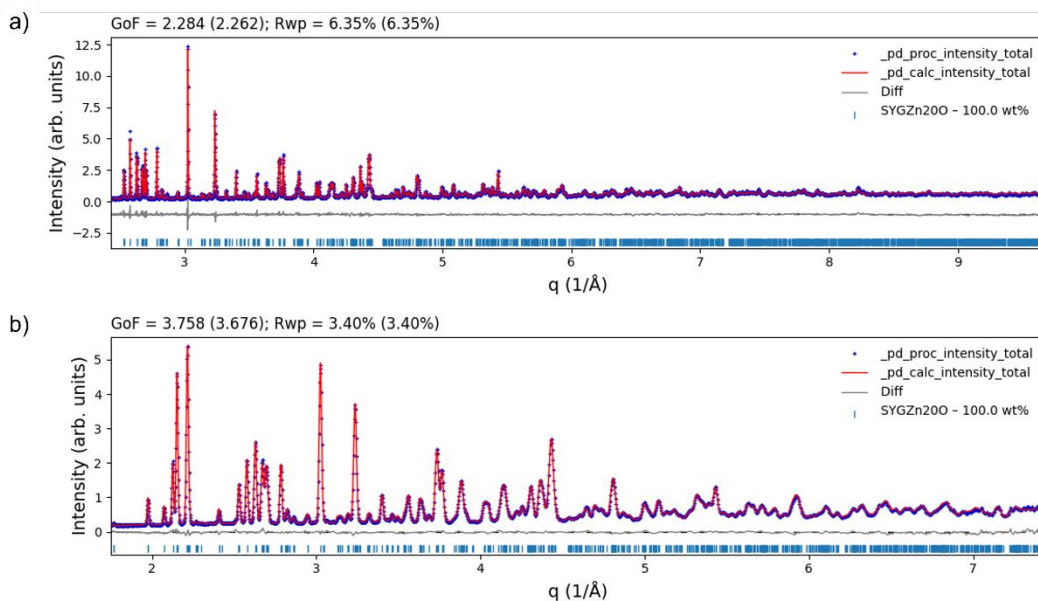


Figure S11. Multibank Rietveld refinement against the NPD patterns of $\text{Sr}_3\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$ collected on HRPD a) backscattering bank b) 90° bank on HRPD. Overall Rwp = 3.25%, GOF = 2.57.

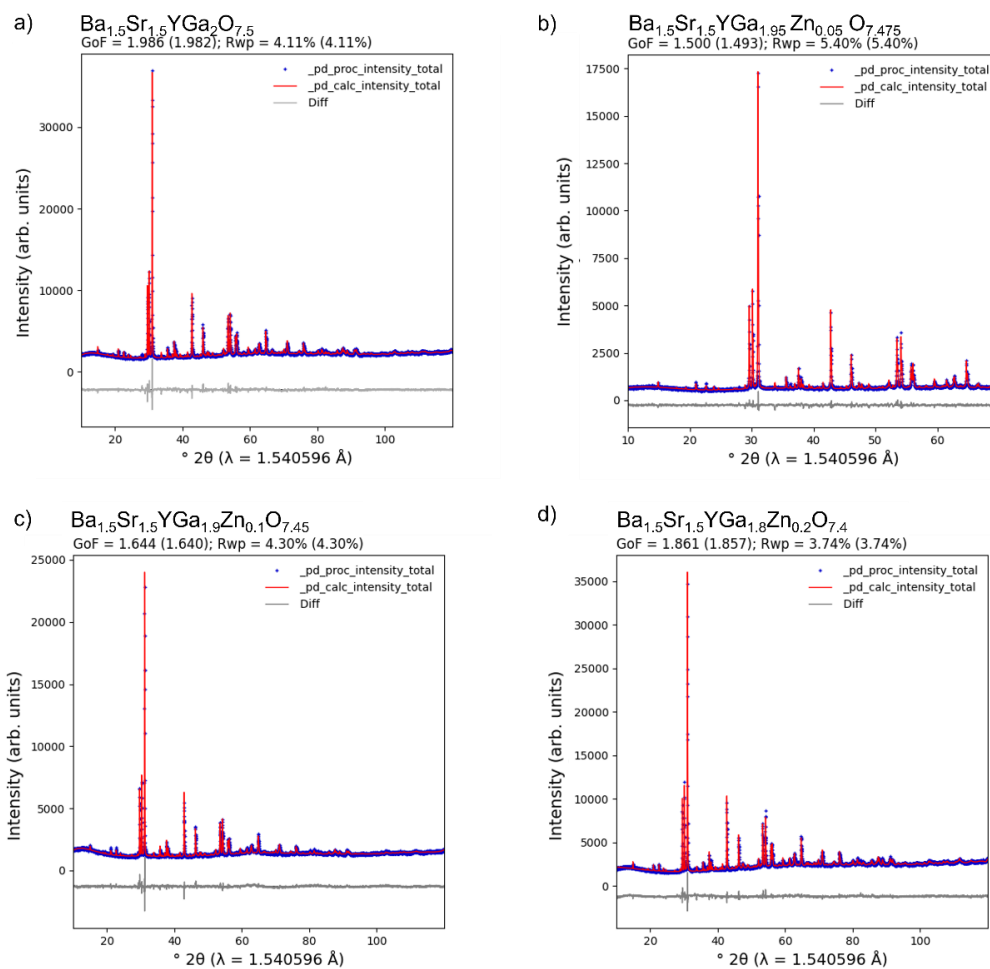


Figure S12. Final Rietveld fits to PXRD data of $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{2-x}\text{Zn}_x\text{O}_{7.5-x/2}$ compounds a) $x = 0$ b) $x = 0.05$ c) $x = 0.1$ d) $x = 0.2$ in space group $P2_1/c$.

Table S2. Crystallographic data for room temperature $\text{Sr}_3\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$ with unit-cell parameters $a = 17.7254(3)$ Å $b = 5.83508(8)$ Å $c = 7.7671(1)$ Å and $\beta = 90.1544(9)^\circ$ in space group $C2$.

Atom	Site	x	y	z	Occ.	$B_{\text{iso}}/\text{\AA}^2$
Sr1	$2a$	0	0.065(1)	0	1	1.4(2)
Sr2	$2b$	0	0.0729(9)	0.5	1	0.8(2)
Sr3	$4c$	0.1698(2)	0.4643(9)	0.9789(5)	1	2.02(9)
Sr4	$4c$	0.1741(2)	0.4671(9)	0.5099(4)	1	1.54(7)
Y1	$4c$	0.3442(1)	0.4767(9)	0.7508(5)	1	0.79(5)
Ga1	$4c$	0.0132(2)	0.5229(4)	0.2373(5)	0.9	1.71(8)
Zn1	$4c$	0.0132(2)	0.5229(4)	0.2372(5)	0.1	1.71(8)
Ga2	$4c$	0.3129(1)	0.4670(5)	0.2441(5)	0.9	0.60(5)
Zn2	$4c$	0.3129(1)	0.4670(5)	0.2441(5)	0.1	0.60(5)
O1	$2a$	0	0.493(3)	0	0.5	1.6(2)
O1a	$4c$	0.0406(8)	0.466(4)	0.949(2)	0.25	1.6(2)
O2	$4c$	0.3605(3)	0.495(1)	0.0379(5)	1	1.8(1)
O3	$4c$	0.3508(3)	0.476(2)	0.4664(6)	1	2.0(1)
O4	$4c$	0.03830(2)	0.8240(5)	0.2592(7)	1	1.20(7)
O5	$4c$	0.0909(3)	0.3211(5)	0.2616(9)	1	1.77(8)
O6	$4c$	0.2595(2)	0.1950(6)	0.2391(8)	1	1.27(7)
O7	$4c$	0.2366(2)	0.6954(6)	0.2333(7)	1	0.79(7)
O8	$4c$	0.9230(6)	0.391(2)	0.280(2)	0.5	1.6(2)
O8a	$4c$	0.921(11)	0.399(5)	0.208(3)	0.25	1.6(2)
O8b	$4c$	0.9388(8)	0.407(3)	0.360(3)	0.25	1.6(2)

Table S3. Crystallographic data for room temperature Ba_{1.5}Sr_{1.5}YGa₂O_{7.5} with unit-cell parameters $a = 7.872(12)$ Å $b = 5.9195(9)$ Å $c = 18.077(3)$ Å and $\beta = 89.981(4)^\circ$ in space group $P2_1/c$.

Atom	Site	x	y	z	Occ.	$B_{\text{iso}}/\text{\AA}^2$
Ba1	2e	0	0.200(2)	0.25	0.5	3.8(3)
Ba2	2f	0.5	0.3057(16)	0.25	0.5	0.7(2)
Ba3	4g	0.0109(11)	0.7543(18)	0.0825(4)	0.5	1.9(2)
Ba4	4g	0.4861(10)	0.2406(14)	0.5834(4)	0.5	1.23(17)
Sr1	2e	0	0.200(2)	0.25	0.5	3.8(3)
Sr2	2f	0.5	0.3057(16)	0.25	0.5	0.7(2)
Sr3	4g	0.0109(11)	0.7543(18)	0.0825(4)	0.5	1.9(2)
Sr4	4g	0.4861(10)	0.2406(14)	0.5834(4)	0.5	1.23(17)
Y1	4g	0.2554(8)	0.2537(12)	0.40884(16)	1	0.35(7)
Ga1	4g	0.2548(10)	0.2490(14)	0.06222(14)	1	0.37(7)
Ga2	4g	0.2327(10)	0.7682(13)	0.2654(2)	1	2.84(12)
O1	2e	0	0.770(4)	0.25	1	7.9(4)
O2	4g	0.0339(10)	0.7583(17)	0.6041(5)	1	2.5(2)
O3	4g	0.4663(10)	0.2539(13)	0.1043(4)	1	1.00(18)
O4	4g	0.237(2)	0.0766(17)	0.2941(5)	0.5	0.66(19)
O4a	4g	0.2792(18)	0.0225(19)	0.3185(7)	0.5	0.66(19)
O5	4g	0.252(4)	0.590(2)	0.3443(7)	0.5	1.5(2)
O5a	4g	0.243(3)	0.527(2)	0.3315(10)	0.5	1.5(2)
O6	4g	0.2378(12)	0.4919(12)	0.5031(4)	1	1.43(14)
O7	4g	0.2571(17)	0.0072(15)	-0.0039(5)	1	4.0(2)
O8	4g	0.301(2)	0.336(3)	0.6746(10)	0.5	3.4(3)
O8a	4g	0.333(2)	0.199(3)	0.6780(12)	0.5	3.4(3)

Table S4. Crystallographic data for room temperature Ba_{1.5}Sr_{1.5}YGa_{1.8}Zn_{0.1}O_{7.45} with unit-cell parameters $a = 7.8602(13)$ Å $b = 5.9198(10)$ Å $c = 18.113(3)$ Å and $\beta = 89.999(4)^\circ$ in space group $P2/c$.

Atom	Site	x	y	z	Occ.	$B_{\text{iso}}/\text{\AA}^2$
Ba1	2e	0	0.189(2)	0.25	0.5	3.0(3)
Ba2	2f	0.5	0.3078(17)	0.25	0.5	1.2(2)
Ba3	4g	0.0122(12)	0.7523(18)	0.0848(4)	0.5	2.0(2)
Ba4	4g	0.4869(10)	0.2356(13)	0.5801(4)	0.5	0.89(18)
Sr1	2e	0	0.189(2)	0.25	0.5	3.0(3)
Sr2	2f	0.5	0.3078(17)	0.25	0.5	1.2(2)
Sr3	4g	0.0122(12)	0.7523(18)	0.0848(4)	0.5	2.0(2)
Sr4	4g	0.4869(10)	0.2356(13)	0.5801(4)	0.5	0.89(18)
Y1	4g	0.2541(9)	0.2528(13)	0.40956(19)	1	0.62(8)
Ga1	4g	0.2521(11)	0.2480(14)	0.06182(15)	0.95	0.32(8)
Zn1	4g	0.2521(11)	0.2480(14)	0.06182(15)	0.05	0.32(8)
Ga2	4g	0.2396(12)	0.7645(13)	0.2654(2)	0.95	3.02(13)
Zn2	4g	0.2396(12)	0.7645(13)	0.2654(2)	0.05	3.02(13)
O1	2e	0	0.762(6)	0.25	0.5	3.4(5)
O1a	4g	0.014(5)	0.824(5)	0.2161(14)	0.25	3.4(5)
O2	4g	0.0339(13)	0.756(2)	0.6030(6)	1	3.6(3)
O3	4g	0.4624(9)	0.2513(12)	0.1051(4)	1	0.3(15)
O4	4g	0.276(2)	0.0778(19)	0.2863(6)	0.5	0.7(2)
O4a	4g	0.225(2)	0.051(2)	0.3151(7)	0.5	0.7(2)
O5	4g	0.255(3)	0.5855(19)	0.3441(6)	0.5	0.6(2)
O5a	4g	0.274(2)	0.514(2)	0.3281(8)	0.5	0.6(2)
O6	4g	0.2509(15)	0.4911(11)	0.5018(3)	1	1.10(14)
O7	4g	0.2399(17)	0.0121(16)	-0.0039(5)	1	3.8(3)
O8	4g	0.315(2)	0.326(4)	0.6707(13)	0.5	4.0(3)
O8a	4g	0.304(3)	0.168(3)	0.6757(12)	0.5	4.0(3)

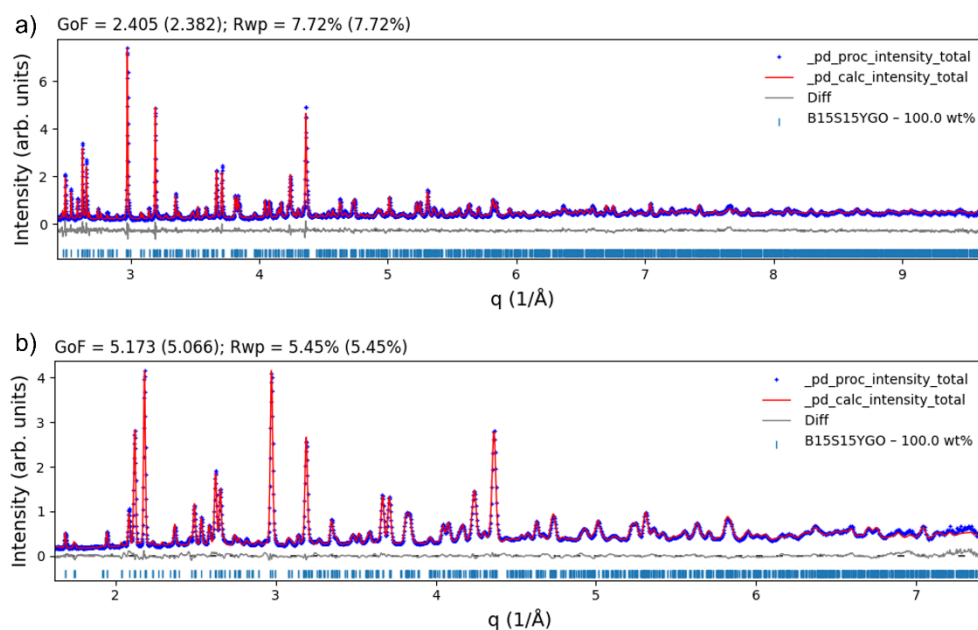


Figure S13. Multibank Rietveld refinement against the room temperature NPD patterns of $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_2\text{O}_{7.5}$ collected on HRPD a) backscattering bank b) 90 ° bank. Overall $R_{\text{wp}} = 5.92\%$, GOF = 3.49.

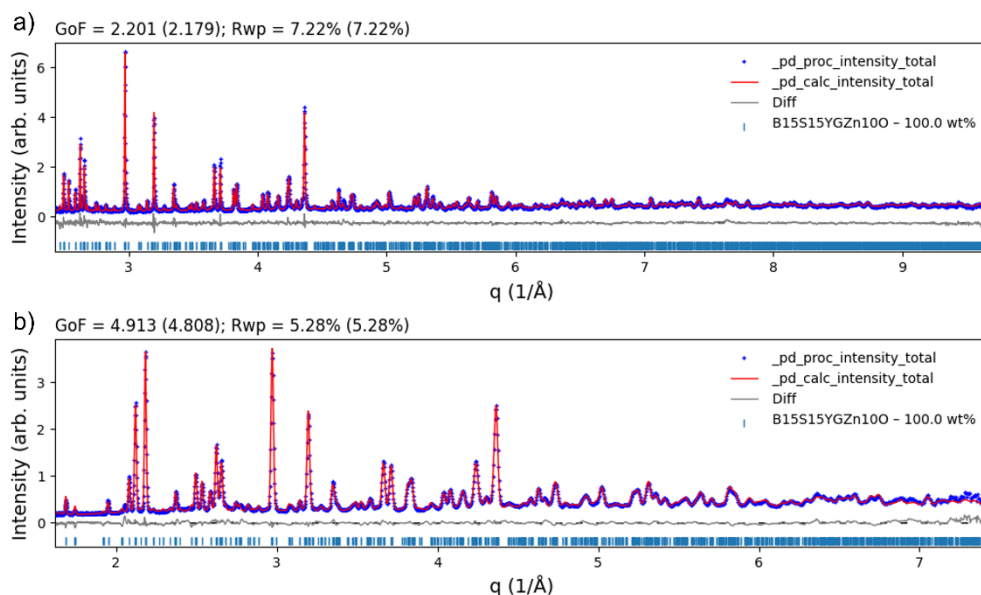


Figure S14. Multibank Rietveld refinement against the room temperature NPD patterns of $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$ collected on HRPD a) backscattering bank b) 90 ° bank. Overall $R_{\text{wp}} = 5.75\%$, GOF = 3.32.

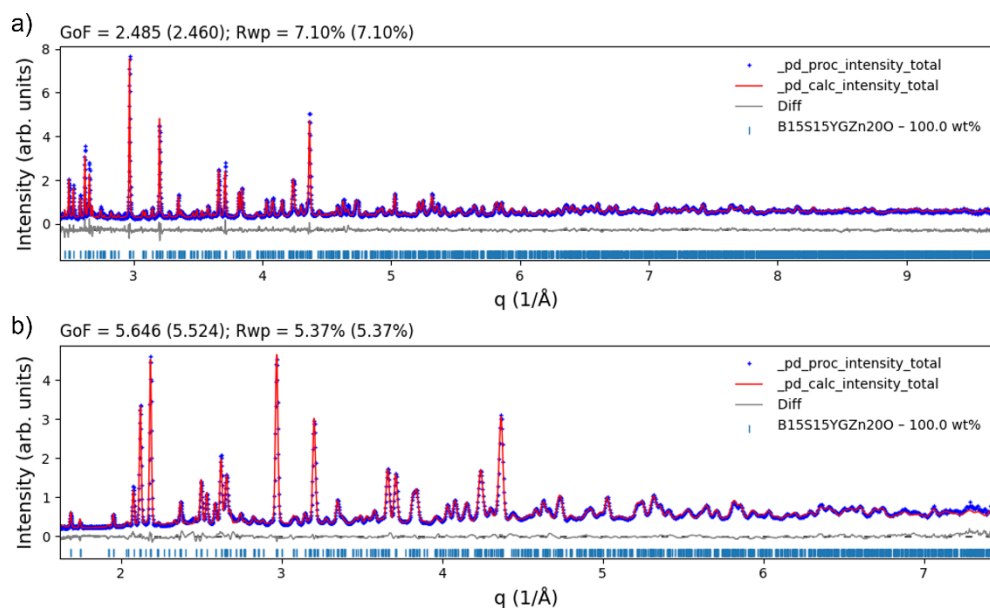


Figure S15. Multibank Rietveld refinement against the room temperature NPD patterns of $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$ collected on HRPD a) backscattering bank b) 90° bank. Overall $R_{\text{wp}} = 5.74\%$, $\text{GOF} = 3.76$.

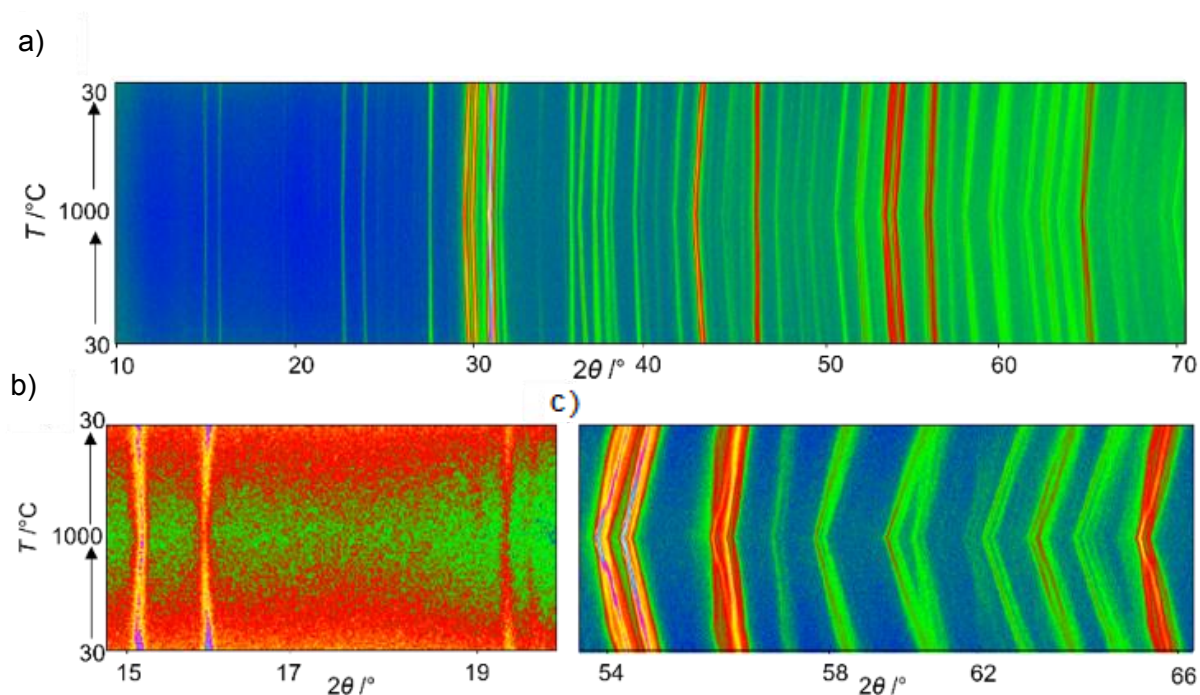


Figure S16. Powder X-ray diffraction patterns of $\text{Sr}_3\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$ on heating and cooling to 1000°C . The heat map is scaled from low intensity (blue) to high intensity (red/white). b) and c) show specific 2θ ranges plotted on logarithmic and square root scales, respectively, to emphasize peak changes at $2\theta \sim 54, 55$ and 65° .

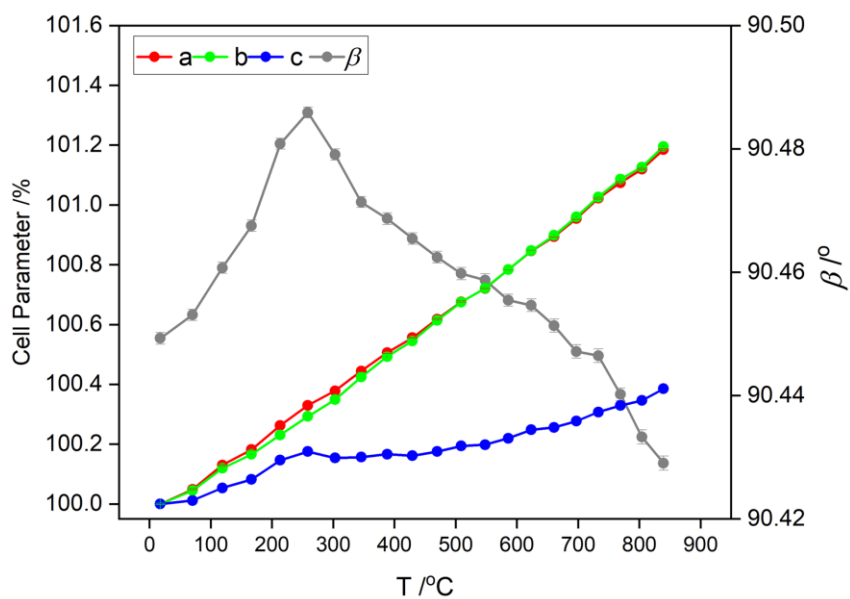


Figure S17. Relative unit-cell parameters and absolute monoclinic angle evolution as a function of temperature for $\text{Sr}_3\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$ extracted from VT-PXRD patterns. Data points are for heating only. Data on cooling were essentially identical.

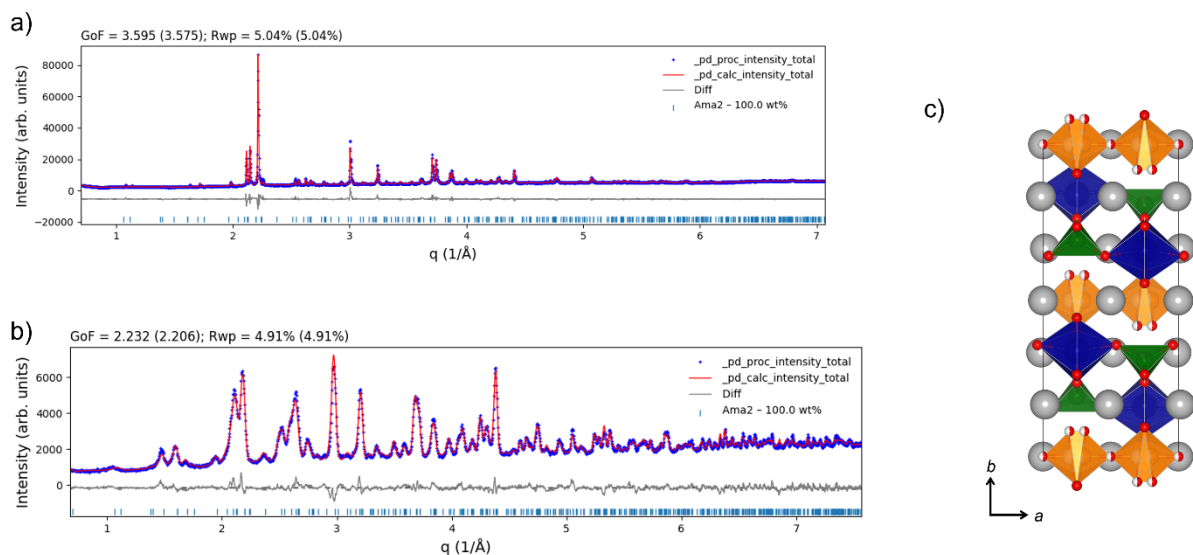


Figure S18. Combined X-ray and neutron Rietveld fit of $\text{Sr}_3\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$ patterns at 850 °C collected on a) a laboratory X-ray source and b) ECHIDNA, $\lambda = 1.622$ Å. c) The final Ama2 model.

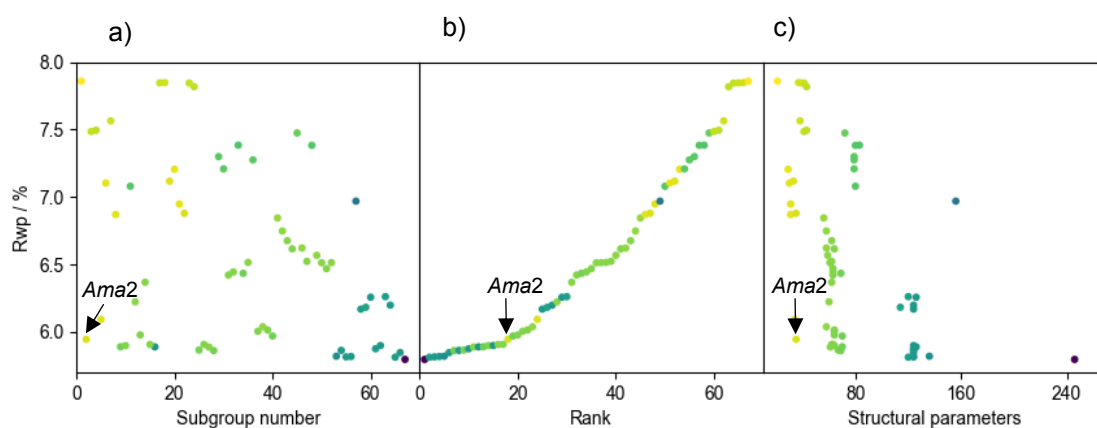


Figure S19. Graphs of R_{wp} against a) Subgroup number b) Rank by lowest R_{wp} c) Number of structural parameters. The colouring of data points from yellow to purple indicates lowest to highest parameter count.

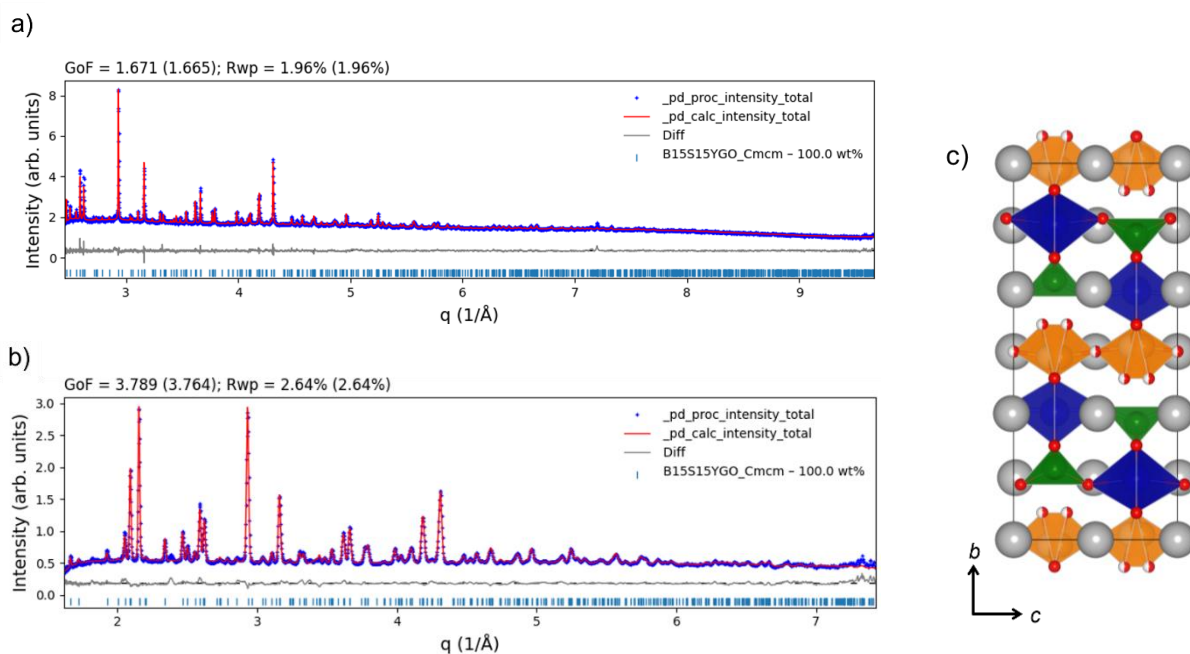


Figure S20. Multibank Rietveld refinement against the NPD patterns of $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_2\text{O}_{7.5}$ at 1000 °C collected on HRPD a) backscattering bank b) 90 ° bank. Overall $R_{wp} = 2.37\%$, $\text{GoF} = 2.55$. There are two broad unfitted peaks at $Q \sim 1.8$ and 2.4 \AA^{-1} , which may correspond to short-range ordering of the $P2_1/a$ or Pc -type. c) The final Cmcm model.

Table S5. Crystallographic data for $\text{Sr}_3\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$ at 1000 °C with unit cell parameters $a = 7.80498(14)$ Å $b = 17.9894(3)$ Å $c = 5.91240(10)$ Å in space group *Ama2*.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	$B_{\text{iso}}/\text{\AA}^2$
Sr1	4	0	0	0.480(11)	1	3.88(13)
Sr2	8	0.0145(5)	0.1667(3)	0.062(11)	1	3.88(13)
Y1	4	0.25	0.3390(2)	0.052(11)	1	1.30(14)
Ga1	4	0.25	0.6941(3)	0.055(11)	0.9	1.99(15)
Zn1	4	0.25	0.6941(3)	0.055(11)	0.1	1.99(15)
Ga2	8	0.2085(10)	0	0.017(11)	0.45	3.0(3)
Zn2	8	0.2085(10)	0	0.017(11)	0.05	3.0(3)
O1	4	0	0	0.04184	0.5	3.3(12)
O2	8	0.0413(12)	0.6429(5)	0.030(11)	1	3.5(2)
O3	4	0.25	0.4064(10)	0.725(11)	1	3.4(3)
O4	4	0.25	0.9445(8)	0.722(11)	1	2.8(3)
O5	4	0.25	0.7624(8)	0.818(11)	1	2.7(3)
O6	4	0.25	0.2366(12)	0.846(11)	1	4.5(4)
O7	8	0.695(5)	0.9190(15)	0.141(12)	0.5	10.3(13)

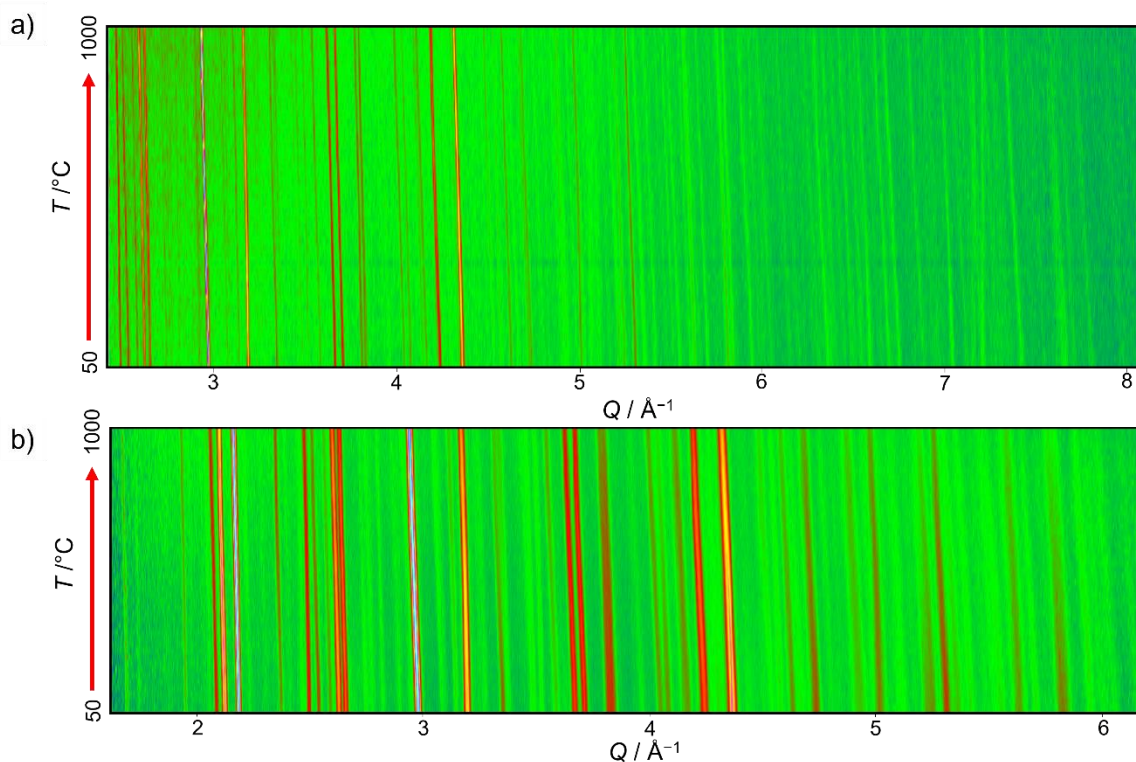


Figure S21. Neutron powder diffraction patterns of $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_2\text{O}_{7.5}$ on heating to 1000 °C from HRPD a) backscattering bank and b) 90-degree bank. The heat map is scaled from low intensity (blue) to high intensity (red/white)

Table S6. Crystallographic data for $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_2\text{O}_{7.5}$ at 1000 °C with unit-cell parameters $a = 5.9984(10)$ Å $b = 18.354(3)$ Å $c = 7.9484(13)$ Å in space group $Cmcm$.

Atom	Site	x	y	z	Occ.	$B_{\text{iso}}/\text{\AA}^2$
Ba1	4	0	0	0	0.5	5.90(15)
Ba2	8	0	0.6648(2)	0.9878(4)	0.5	6.21(9)
Sr1	4	0	0	0	0.5	5.90(15)
Sr2	8	0	0.6648(2)	0.9878(4)	0.5	6.21(9)
Y1	4	0	0.8388(2)	0.75	1	2.63(9)
Ga1	4	0	0.19046(16)	0.75	1	2.68(9)
Ga2	8	0	0.4857(2)	0.7126(6)	0.5	3.51(13)
O1	4	0	0.5	0	0.5	10.2(4)
O2	8	0	0.14656(19)	0.9565(5)	1	6.95(12)
O3	8	0.7518(7)	0.4287(2)	0.75	1	7.11(12)
O4	8	0.2546(8)	0.24940(17)	0.75	1	5.23(12)
O5	8	0	0.5717(4)	0.6752(8)	0.5	9.0(2)

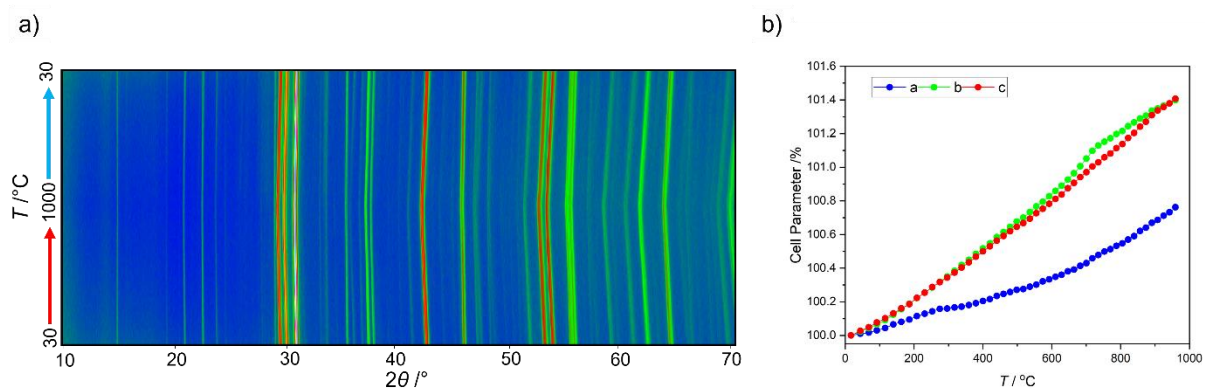


Figure S22. A) Powder X-ray diffraction patterns of $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$ on heating and cooling to 1000 °C. The heat map is scaled from low intensity (blue) to high intensity (red/white). b) The relative unit cell expansion on heating (data on cooling is omitted for clarity but shows good agreement).

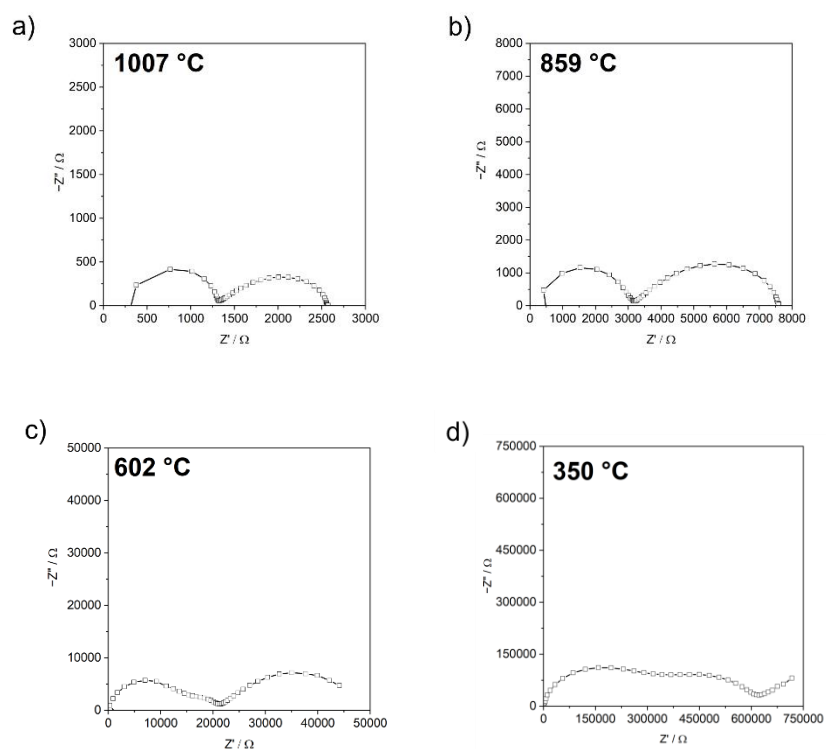


Figure S23. Complex plane plots collected at a) 1007 °C b) 859 °C c) 602 °C d). 350 °C in air for $\text{Sr}_3\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$.

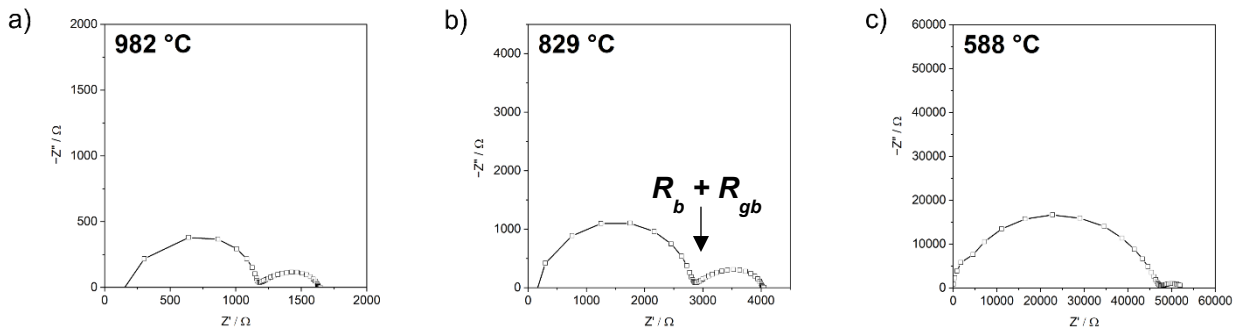


Figure S24. Complex plane plots collected at a) 982 °C b) 829 °C c) 588 °C in air for $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$.

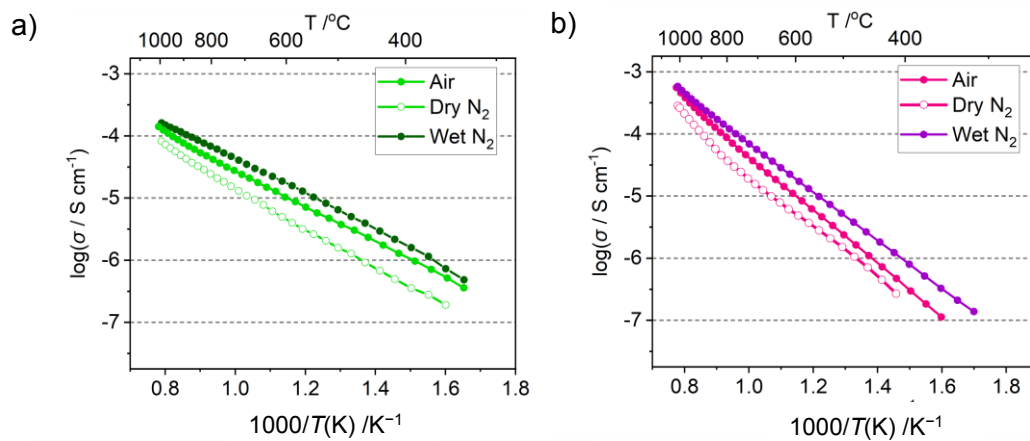


Figure S25. Conductivity of a) $\text{Sr}_3\text{YGa}_{1.95}\text{Zn}_{0.05}\text{O}_{7.475}$ and b) $\text{Sr}_3\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$ under air, wet N_2 and dry N_2 .

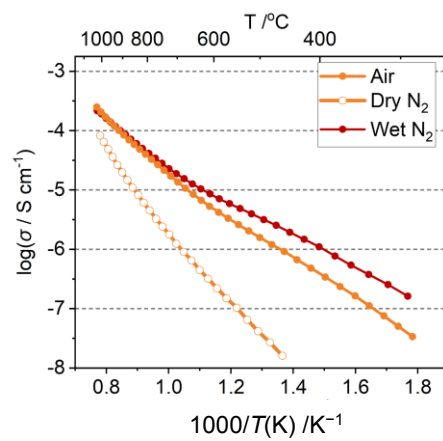


Figure S26. Conductivity of $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$ under air, wet N_2 and dry N_2 .

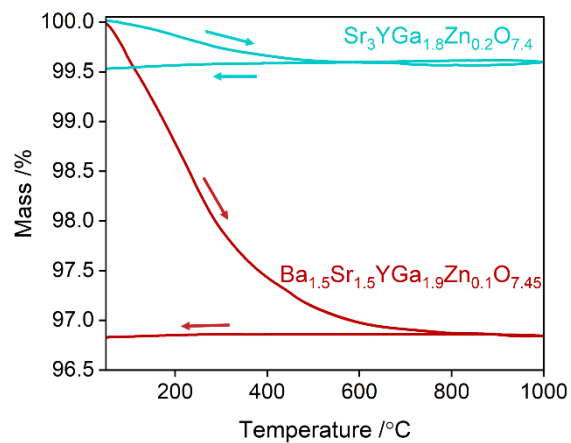


Figure S27. TGA traces on heating and cooling for $\text{Sr}_3\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$ and $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$.

Table S7. Proton transport numbers, t_{H} , calculated for select compounds at 600 and 1000 °C.

Compound	t_{H} @ 600 °C	t_{H} @ 1000 °C
$\text{Sr}_3\text{YGa}_{1.95}\text{Zn}_{0.05}\text{O}_{7.475}$	0.61	0.42
$\text{Sr}_3\text{YGa}_{1.8}\text{Zn}_{0.2}\text{O}_{7.4}$	0.56	0.49
$\text{Ba}_{1.5}\text{Sr}_{1.5}\text{YGa}_{1.9}\text{Zn}_{0.1}\text{O}_{7.45}$	0.96	0.61