Supporting Information

Effects of Al Concentration on the Structure and Conductivity of Lithium Lanthanum Zirconium Oxide

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Nominal	Expected (+20 wt.% Li-excess)	Actual (ICP)
$Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$	$Li_{7.51}Al_{0.25}La_3Zr_2O_{12}$	$Li_{6.43}Al_{0.171}La_{2.90}Zr_{1.93}O_{12-\delta}$
$Li_{5.95}Al_{0.35}La_3Zr_2O_{12}$	$Li_{7.08}Al_{0.35}La_3Zr_2O_{12}$	$Li_{6.18}Al_{0.286}La_{2.92}Zr_{1.95}O_{12-\delta}$
$Li_{5.65}Al_{0.45}La_3Zr_2O_{12}$	$Li_{6.79}Al_{0.45}La_3Zr_2O_{12}$	$Li_{5.93}Al_{0.323}La_{2.93}Zr_{1.93}O_{12-\delta}$

Table S1. Nominal or intended composition, the expected composition assuming no Li-loss of excess Li, and the actual composition as measured by ICP and adjusted to the weight fraction of cubic LLZO as determined by Rietveld refinement. In all ICP measurements our calibration curves for each element have R values of at least 0.998, all samples measured were in the range of the calibration curves, and each element concentration is at least three orders of magnitude above the detection limit for the elements of interest.

To determine the source of the decreased Al, first the alumina precursor was checked. $Al(OH)_3$ is a precursor in the processing of Al_2O_3 and is both 24 g mol^{-1} lighter than alumina and has 1 less mol of Al per mol of compound. Therefore, if there is any residual $Al(OH)_3$ from the production process, the actual amount of Al added as a precursor would be lower than expected.

1 g of $Al(OH)_3$ would result in 65% of the mol of Al that would be expected if 1 g of Al_2O_3 were added. Since, in the case of the LLZO-Al0.17 composition, 68% of the Al concentration is present as compared to the expected 0.25 mol, nearly all of the Al_2O_3 would have to be $Al(OH)_3$. To determine if this was the case, the Al_2O_3 precursor was heated to 300 ˚C, which is above the 180 ˚C decomposition temperature of $Al(OH)_3$ to Al_2O_3, for 24 hours. With a starting mass of 1.0156 g, the expected final mass of 0.6637 g would need to remain for full conversion from $Al(OH)_3$ to Al_2O_3. However, after weighing, only 0.0304 g was lost. Therefore, $Al(OH)_3$ impurities in the Al_2O_3 precursor are not likely to be the source of decreased composition.

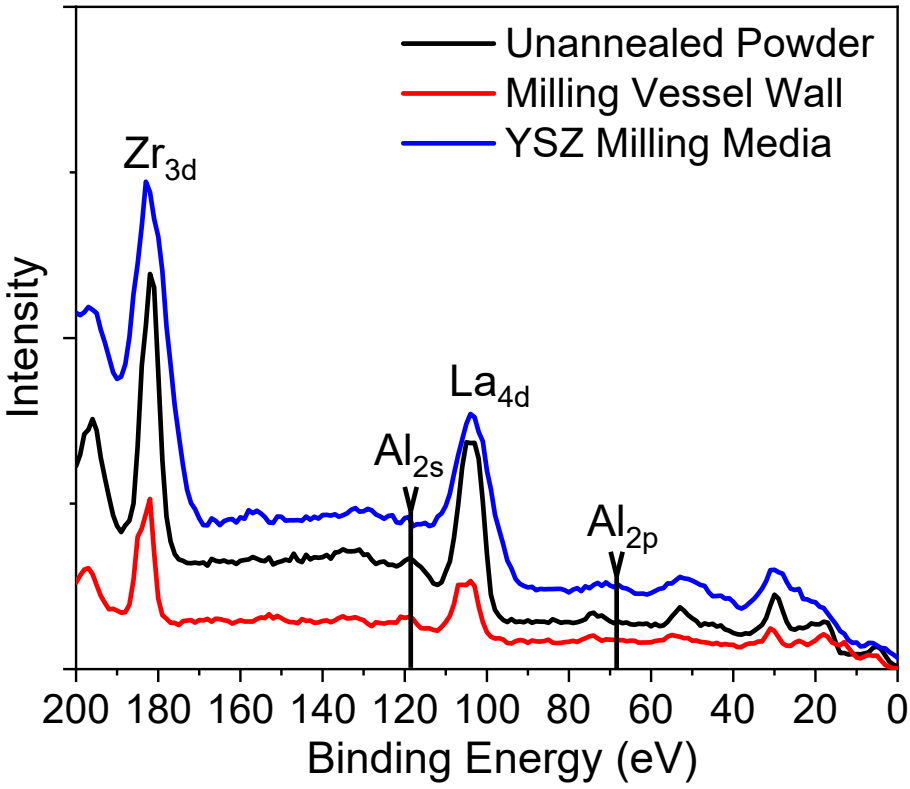


Figure S1. XPS of LLZO-Al powder, milling jar, and yttria stabilized zirconia milling media.

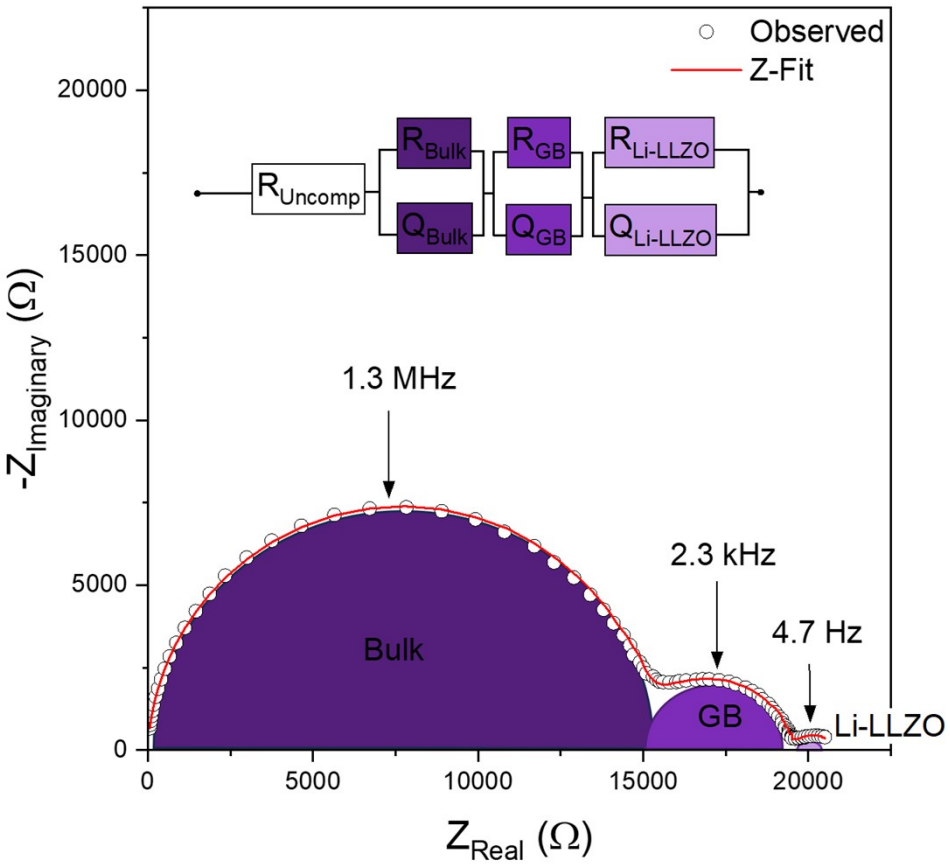


Figure S2. Representative Nyquist plot. LLZO-Al0.17 at a nominal temperature of -30 °C. Open circles are the observed spectra and red are the Z-fit as determined by the equivalent circuit in the inset of the graph. Equivalent circuit elements and semicircles are labeled with the corresponding transport mechanism. Semicircles are intended to guide the eye. Bulk (dark purple) corresponds to Li-ion transport through the grains, GB (middle purple) is Li-ion transport through the grain boundaries, and Li-LLZO (light purple) is Li-ion transport across the LLZO|Li electrode interface. Each semicircle is labeled with the characteristic frequency at the apex. The assignment of the equivalent circuit elements as grain, grain boundary, and electrode interface was guided by several previous works on oxide ionic conductors, Al-doped LLZO, and, specifically, hot-pressed LLZO.[1–10]

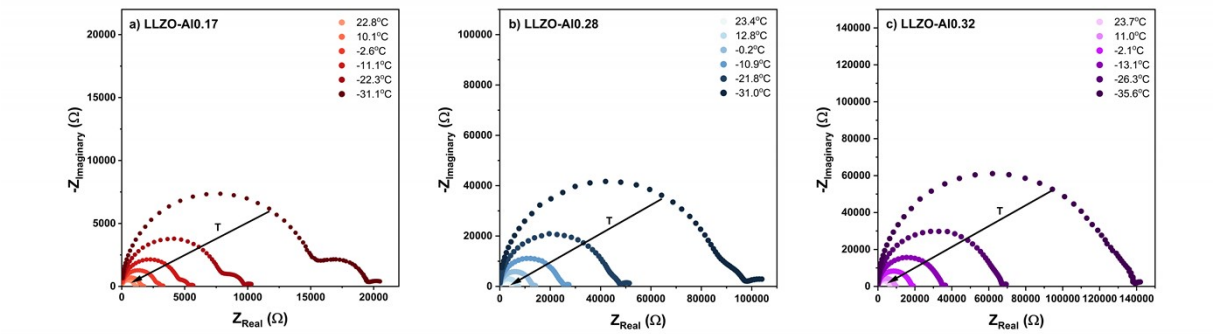


Figure S3. Representative Nyquist plots used for Arrhenius measurements to determine activation energy of each composition. a) LLZO-Al0.17, b) LLZO-Al0.28, c) LLZO-Al0.32. Darker colors indicate lower temperatures while lighter colors indicate higher temperatures.

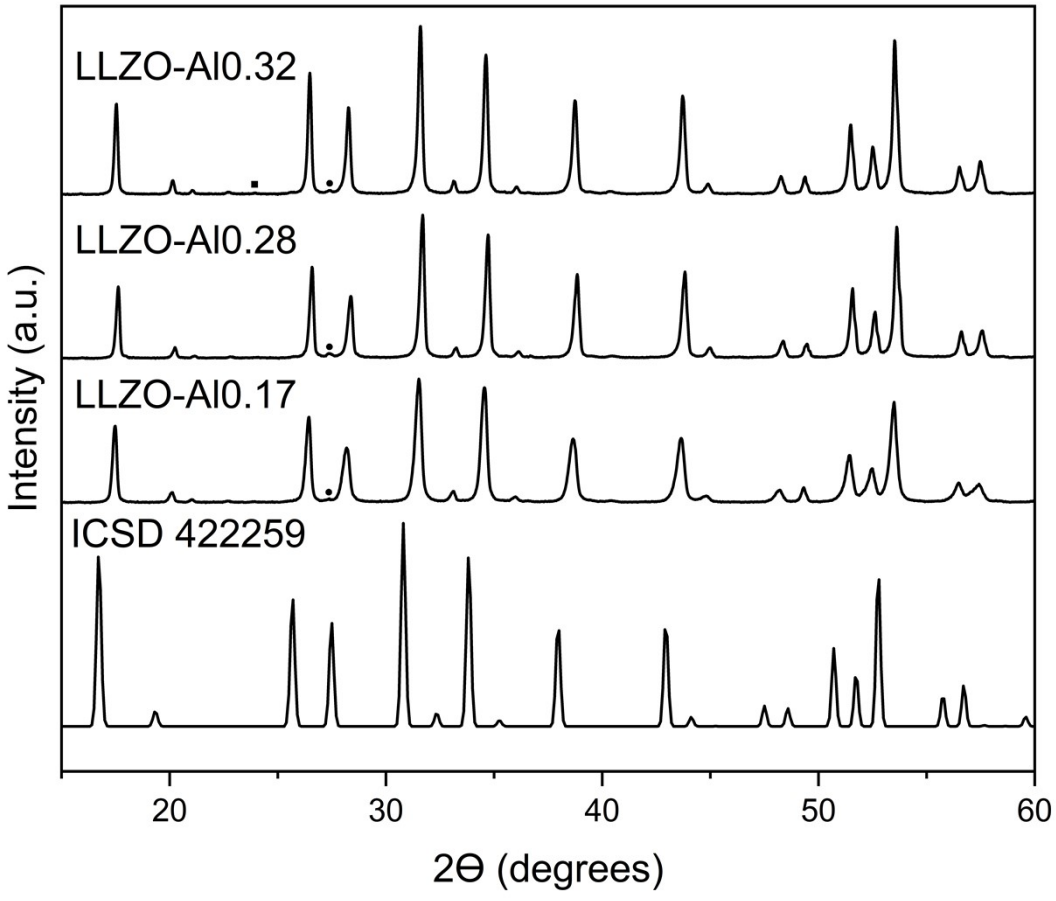


Figure S4. XRD patterns obtained from each composition as well as ICSD 422259 for cubic LLZO. The black circle indicates the most prominent peak for Li_2ZrO_3. The black square marks the most prominent peak for $LaAlO_3$. Shift in peaks of the samples observed in this work compared to the ICSD file are likely due to differences in z-height alignment between the instruments used. The increased width of the peaks observed compared to the ICSD file

can come from several sources, such as the stress associated with the hot-pressing method, smaller particle sizes, or instrument dependent peak broadening.

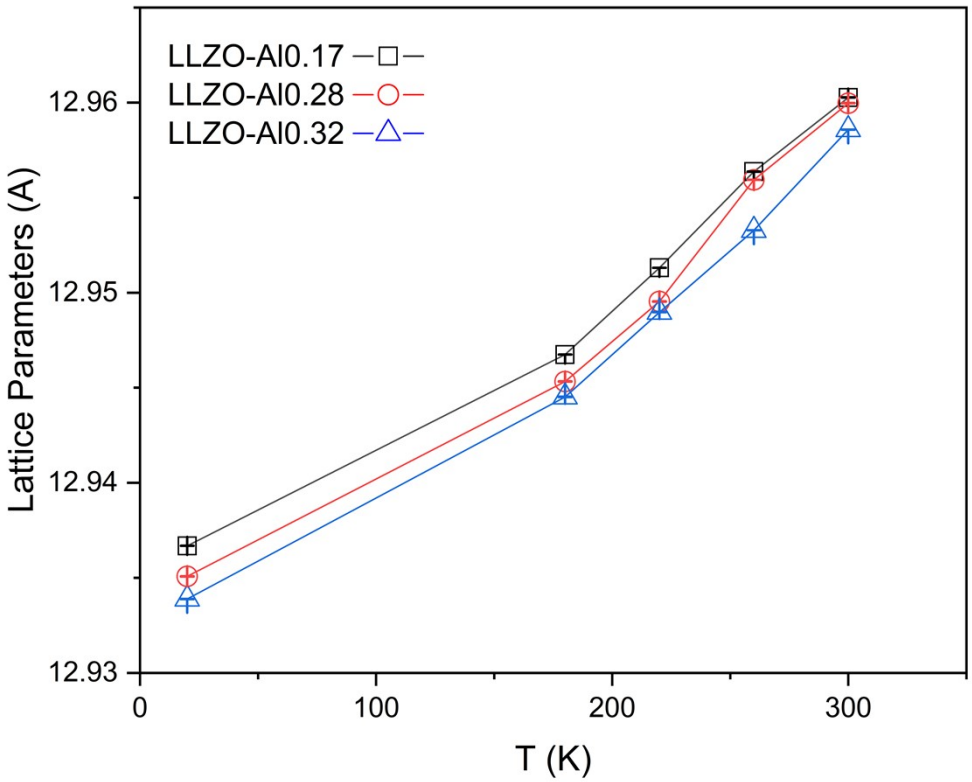
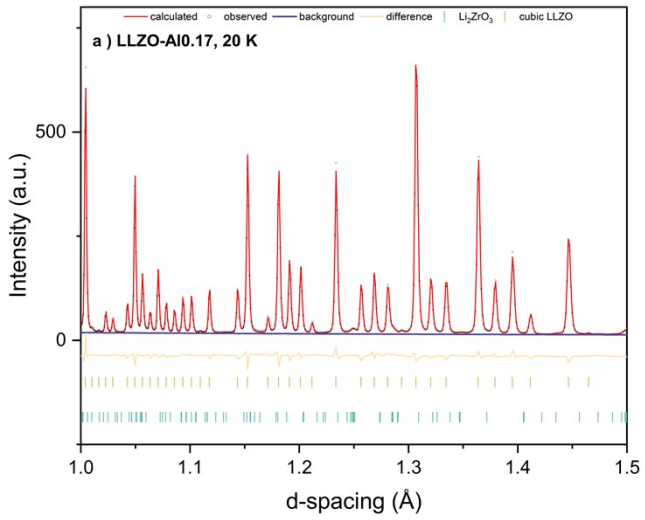
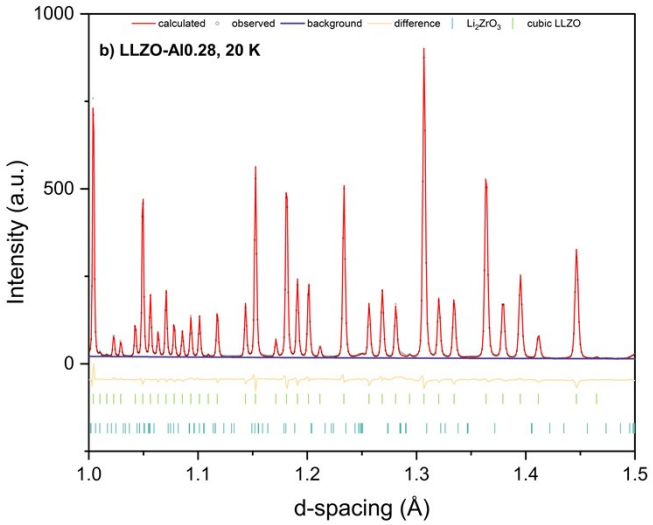


Figure S5. Lattice parameters as a function of temperature.


calculated
observed
background
difference
Li_2ZrO_3
cubic LLZO
a) LLZO-Al0.17, 20 K
Intensity (a.u.)
500
0
1.0
1.1
1.2
1.3
1.4
1.5
d-spacing (Å)


calculated
observed
background
difference
Li_2ZrO_3
cubic LLZO
b) LLZO-Al0.28, 20 K
Intensity (a.u.)
1000
500
0
1.0
1.1
1.2
1.3
1.4
1.5
d-spacing (Å)

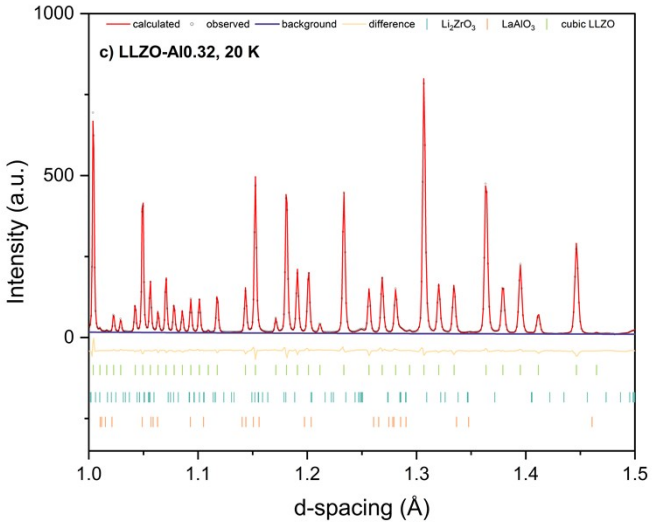

calculated
observed
background
difference
Li_2ZrO_3
$LaAlO_3$
cubic LLZO
c) LLZO-Al0.32, 20 K
Intensity (a.u.)
1000
500
0
1.0
1.1
1.2
1.3
1.4
1.5
d-spacing (Å)

Figure S6. Neutron powder diffraction for a) LLZO-Al0.17, b) LLZO-Al0.28, and c) LLZO-Al0.32 at 20 K to show quality of fit between the neutron diffraction pattern and the calculated refined model from Rietveld refinement. Red lines are the pattern calculated using the refined model, open black circles are the observed neutron diffraction pattern, the purple line is the background, the yellow line is the difference curve, the green dash marks are the expected locations for cubic LLZO, the teal blue dash marks are the expected locations for Li_2ZrO_3, and the orange dash marks are the expected locations for $LaAlO_3$ (shown where applicable).

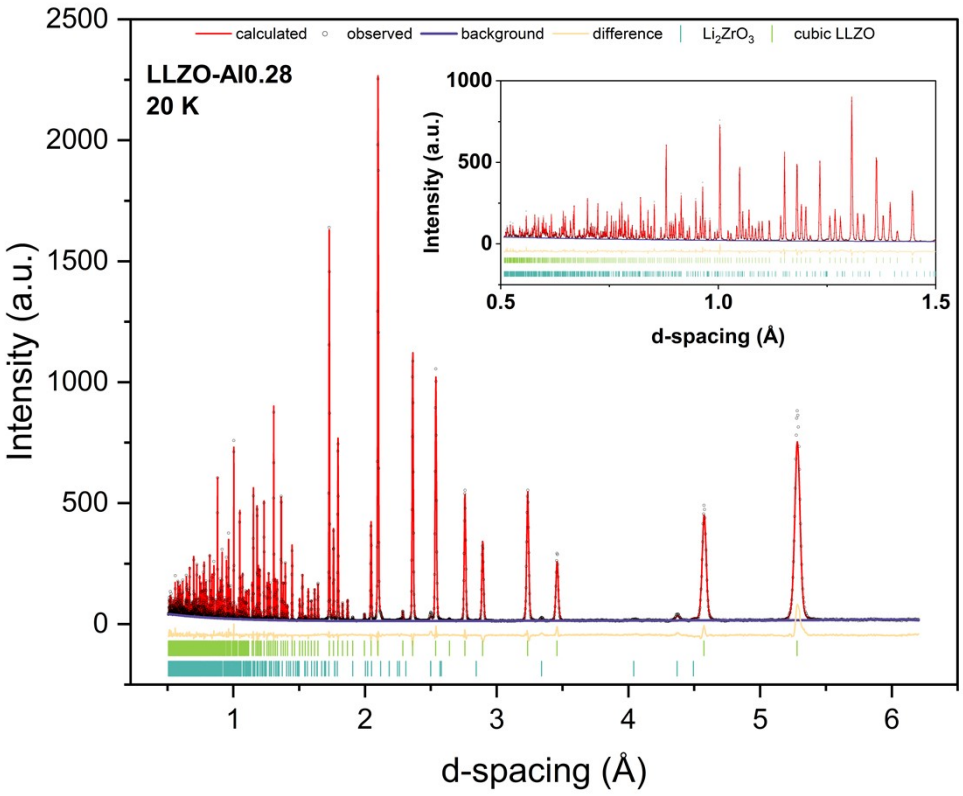


Figure S7. Rietveld refinement results and neutron powder diffraction (NPD) for LLZO-Al0.28 at 20 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}

Li1	**24d**	**0.375**	**0**	**0.25**	**0.4500**	**3.75(24)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.0953**	**3.75(24)**
Li2	**96h**	**0.09704(25)**	**0.18701(28)**	**0.42549(27)**	**0.4025**	**0.91(6)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9979(18)**	**0.483(8)**
Zr1	**16a**	**0**	**0**	**0**	**0.9951(20)**	**0.401(10)**
O1	**96h**	**0.09984(4)**	**0.19603(4)**	**0.28212(4)**	**0.9977(16)**	**0.826(8)**

Table S2. Structural Refinement 20 K LLZO-Al0.28. R_{wp} = 4.729%, lattice parameter a = 12.93508(7) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S2 or in the discussion.

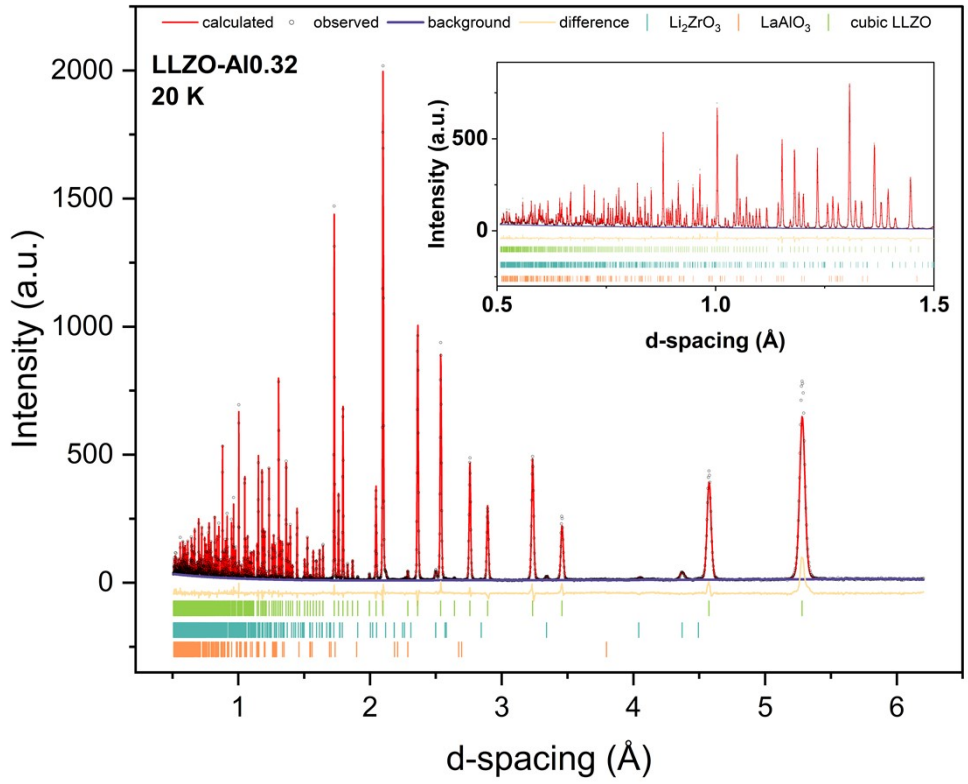


Figure S8. Rietveld refinement results and NPD for LLZO-Al0.32 at 20 K.

Element	**Wyckoff**	**x**	**y**	**z**	**Fraction**	**100*U_{iso}**

	Position					
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4500**	**3.70(24)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.1077**	**3.70(24)**
Li2	**96h**	**0.09699(23)**	**0.18697(26)**	**0.42515(25)**	**0.3817**	**0.78(6)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9973(16)**	**0.384(7)**
Zr1	**16a**	**0**	**0**	**0**	**0.9952(19)**	**0.302(9)**
O1	**96h**	**0.09982(4)**	**0.19605(4)**	**0.28206(3)**	**0.9981(15)**	**0.730(7)**

Table S3. Structural Refinement 20 K LLZO-Al0.32. R_{wp} = 4.643%, lattice parameter a = 12.93389(7) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S3 or in the discussion.

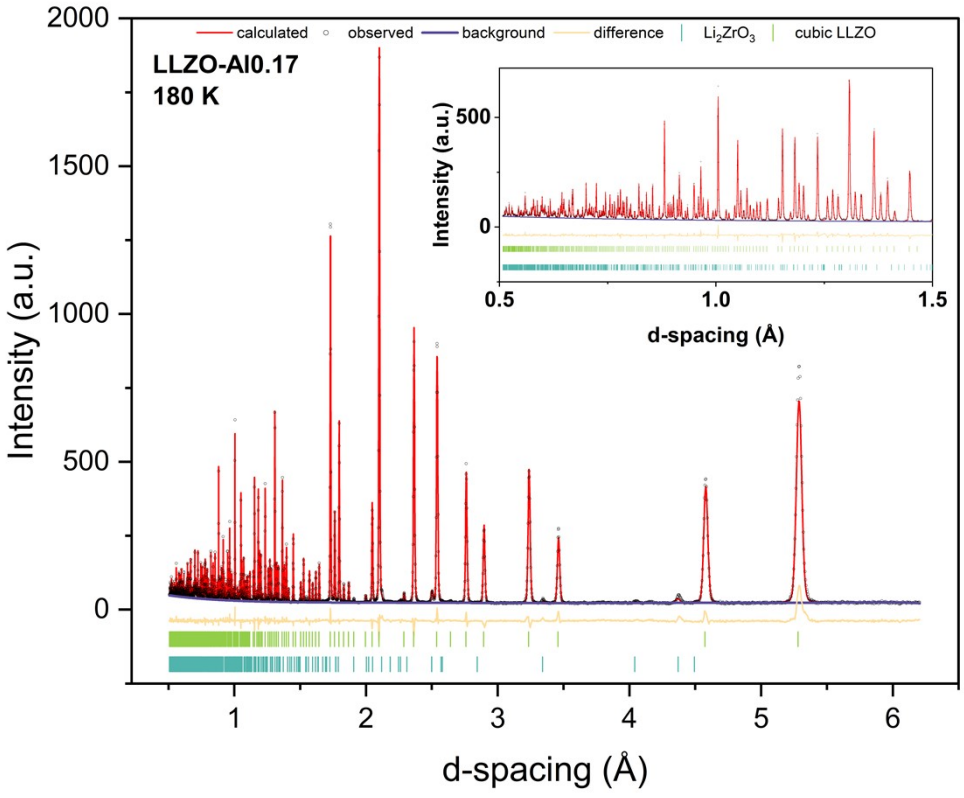


Figure S9. Rietveld refinement results and NPD for LLZO-Al0.17 at 180 K.

Element	Wyckoff Position	x	y	z	Fraction	$100*U_{iso}$
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4500**	**2.58(16)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.0570**	**2.58(16)**
Li2	**96h**	**0.09652(27)**	**0.18702(30)**	**0.42498(29)**	**0.4233**	**1.02(7)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9998(20)**	**0.605(10)**
Zr1	**16a**	**0**	**0**	**0**	**0.9960(23)**	**0.503(12)**
O1	**96h**	**0.09997(4)**	**0.19594(5)**	**0.28208(4)**	**0.9977(19)**	**0.899(9)**

Table S4. Structural Refinement 180 K LLZO-Al0.17. R_{wp} = 4.280%, lattice parameter a = 12.94675(14) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S4 or in the discussion.

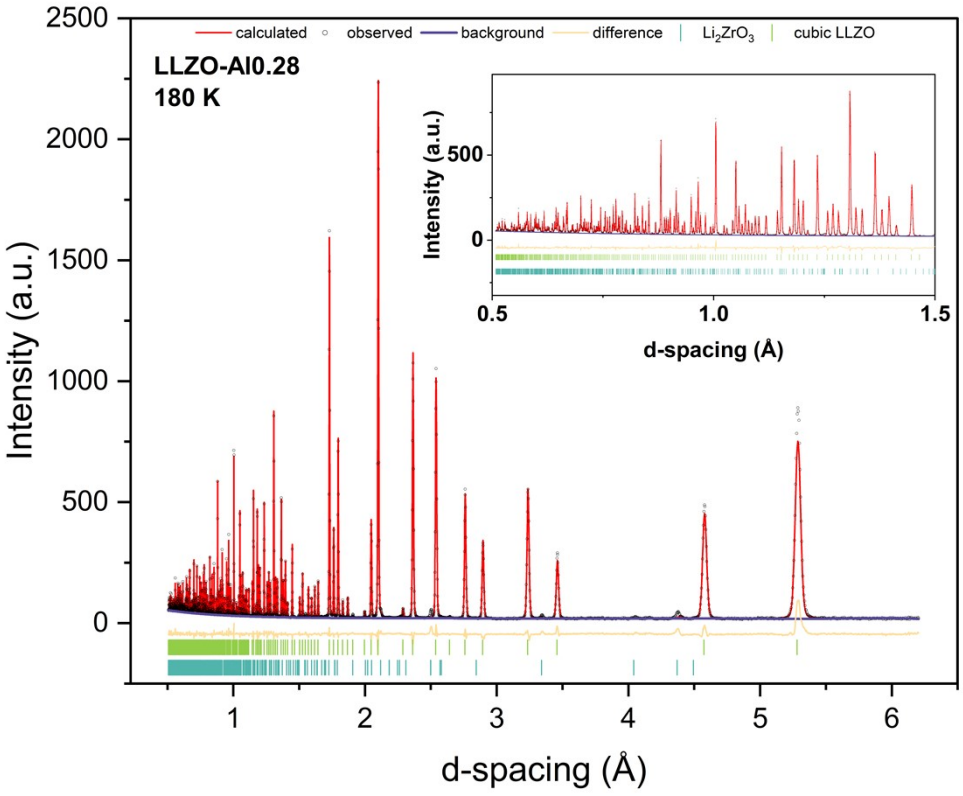


Figure S10. Rietveld refinement results and NPD for LLZO-Al0.28 at 180 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4500**	**3.95(27)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.0953**	**3.95(27)**
Li2	**96h**	**0.09683(27)**	**0.18676(30)**	**0.42497(29)**	**0.4025**	**1.12(7)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9978(19)**	**0.623(9)**
Zr1	**16a**	**0**	**0**	**0**	**0.9956(22)**	**0.512(11)**
O1	**96h**	**0.09984(4)**	**0.19614(4)**	**0.28204(4)**	**0.9975(18)**	**0.950(8)**

Table S5. Structural Refinement 180 K LLZO-Al0.28. R_{wp} = 4.566%, lattice parameter a = 12.94533(8) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S5 or in the discussion.

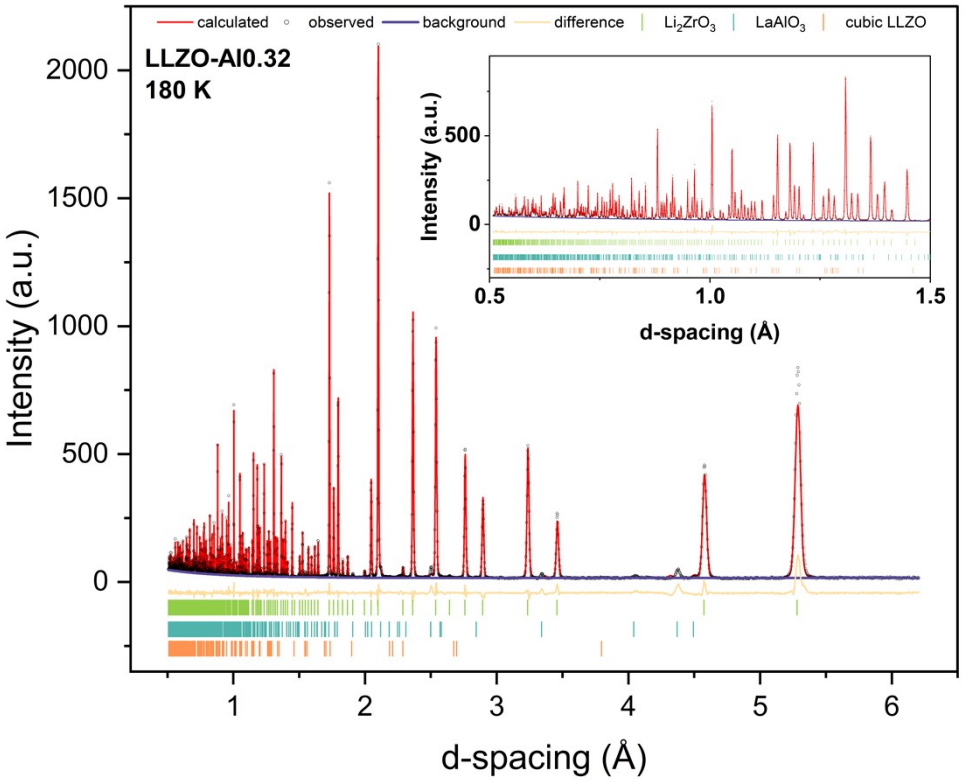


Figure S11. Rietveld refinement results and NPD for LLZO-Al0.32 at 180 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4250**	**3.69(30)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.1077**	**3.69(30)**
Li2	**96h**	**0.09684(27)**	**0.18710(31)**	**0.42475(29)**	**0.3880**	**1.10(7)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9979(19)**	**0.544(8)**
Zr1	**16a**	**0**	**0**	**0**	**0.9956(23)**	**0.416(10)**
O1	**96h**	**0.09980(4)**	**0.19617(4)**	**0.28205(4)**	**0.9972(18)**	**0.872(8)**

Table S6. Structural Refinement 180 K LLZO-Al0.32. R_{wp} = 4.829%, lattice parameter a = 12.94452(7) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S6 or in the discussion.

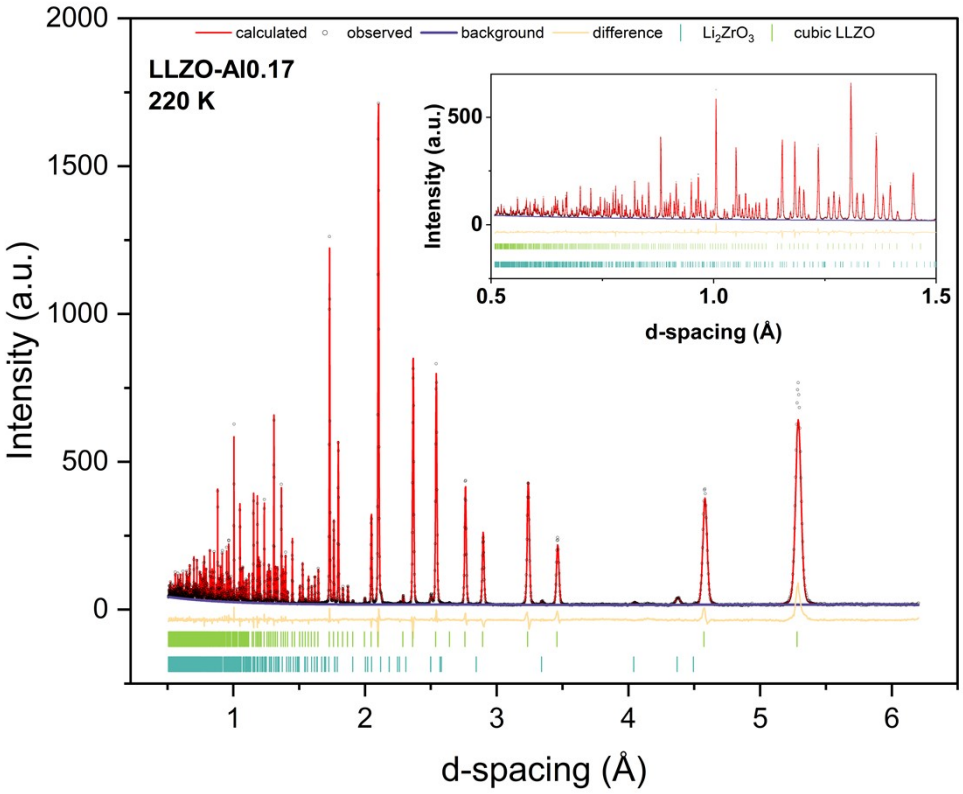


Figure S12. Rietveld refinement results and NPD for LLZO-Al0.17 at 220 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4500**	**2.71(15)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.0570**	**2.71(15)**
Li2	**96h**	**0.09695(25)**	**0.18719(29)**	**0.42501(27)**	**0.4233**	**1.08(7)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9983(19)**	**0.653(9)**

Zr1	**16a**	**0**	**0**	**0**	**0.9945(22)**	**0.538(11)**
O1	**96h**	**0.09998(4)**	**0.19600(4)**	**0.28203(4)**	**0.9960(18)**	**0.948(9)**

Table S7. Structural Refinement 220 K LLZO-Al0.17. R_{wp} = 4.368%, lattice parameter a = 12.95131(14) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S7 or in the discussion.

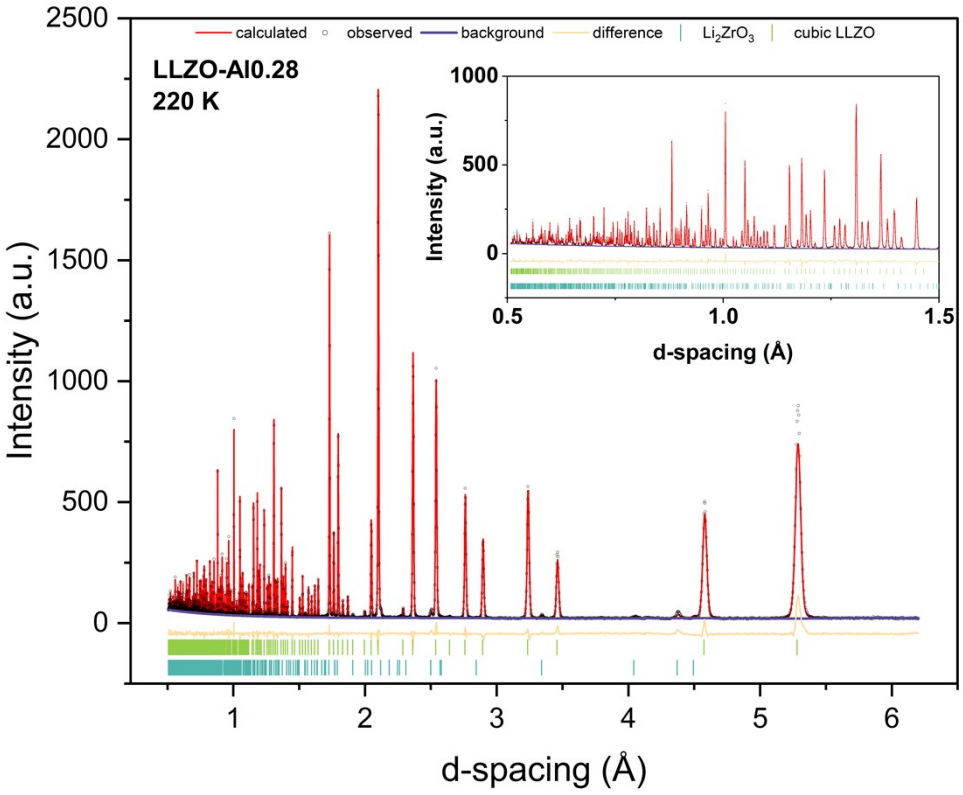


Figure S13. Rietveld refinement results and NPD for LLZO-Al0.28 at 220 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4500**	**4.22(24)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.0953**	**4.22(24)**

Li2	**96h**	**0.09700(24)**	**0.18701(28)**	**0.42503(26)**	**0.4025**	**1.17(6)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9981(17)**	**0.645(8)**
Zr1	**16a**	**0**	**0**	**0**	**0.9959(20)**	**0.537(10)**
O1	**96h**	**0.09990(4)**	**0.19619(4)**	**0.28204(4)**	**0.9965(16)**	**0.985(8)**

Table S8. Structural Refinement 220 K LLZO-Al0.28. R_{wp} = 3.973%, lattice parameter a = 12.94954(8) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S8 or in the discussion.

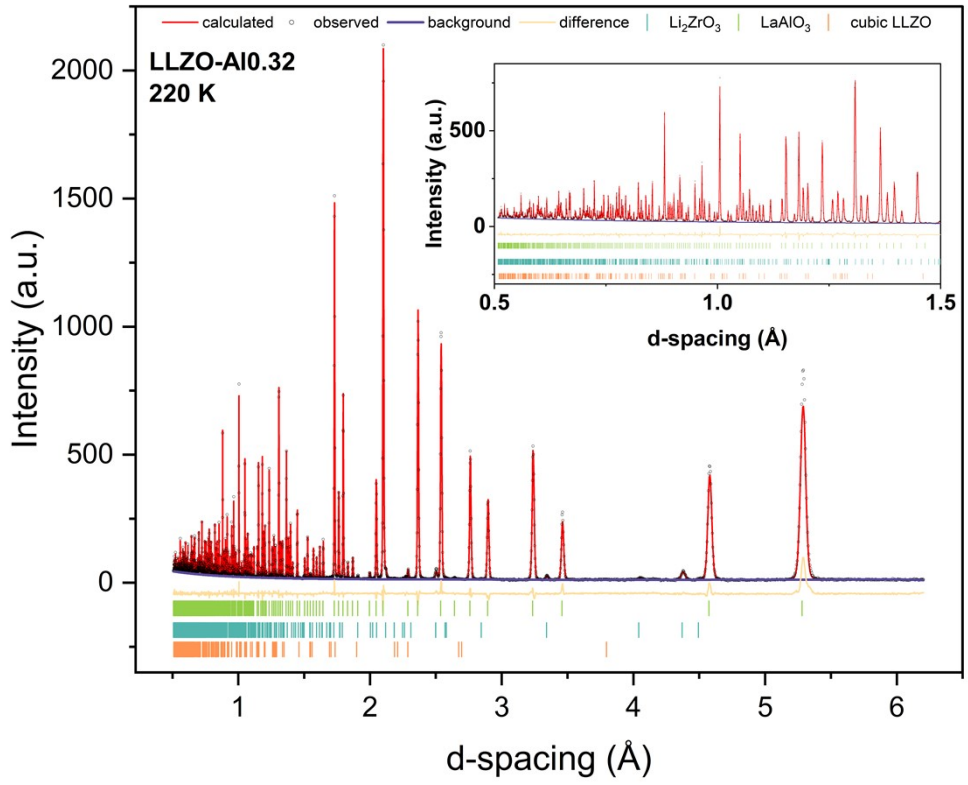


Figure S14. Rietveld refinement results and NPD for LLZO-Al0.32 at 220 K.

Element	**Wyckoff Position**	**x**	**y**	**z**	**Fraction**	**100*U_{iso}**

Li1	**24d**	**0.375**	**0**	**0.25**	**0.4500**	**4.35(27)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.1077**	**4.35(27)**
Li2	**96h**	**0.09753(23)**	**0.18695(26)**	**0.42474(25)**	**0.3817**	**0.96(6)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9980(16)**	**0.574(7)**
Zr1	**16a**	**0**	**0**	**0**	**0.9950(19)**	**0.446(9)**
O1	**96h**	**0.09987(3)**	**0.19620(4)**	**0.28203(3)**	**0.9969(15)**	**0.908(7)**

Table S9. Structural Refinement 220 K LLZO-Al0.32. R_{wp} = 4.280%, lattice parameter a = 12.94898(7) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S9 or in the discussion.

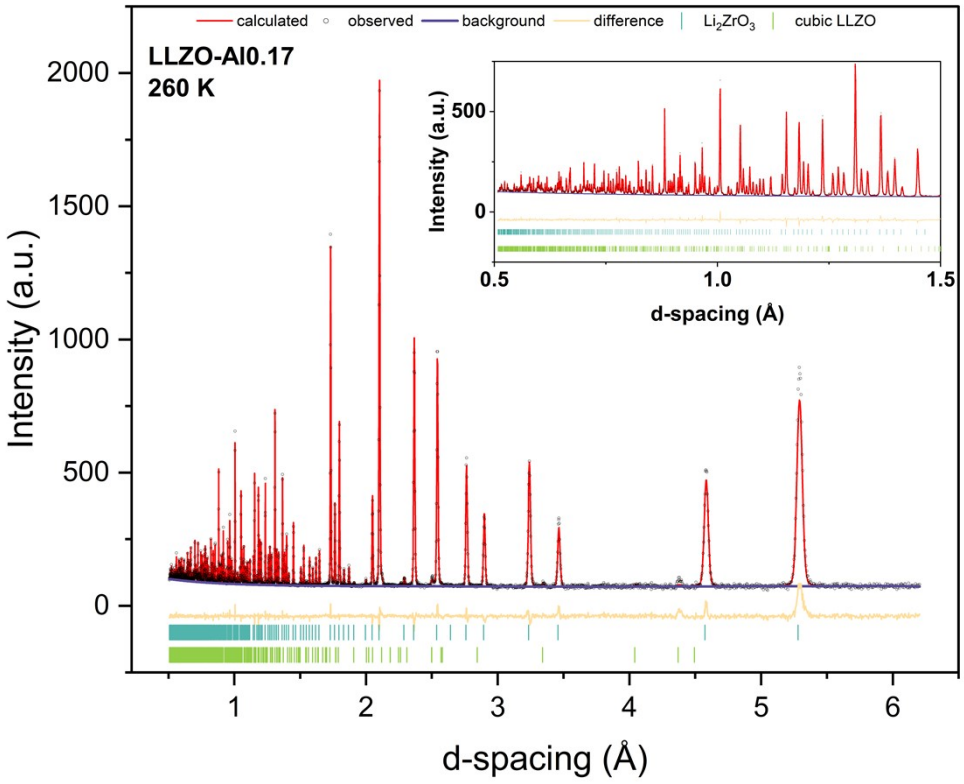


Figure S15. Rietveld refinement results and NPD for LLZO-Al0.17 at 260 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4250**	**2.81(21)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.0570**	**2.81(21)**
Li2	**96h**	**0.09698(30)**	**0.1867(3)**	**0.4247(3)**	**0.4295**	**1.25(8)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9983(23)**	**0.700(11)**
Zr1	**16a**	**0**	**0**	**0**	**0.9936(27)**	**0.579(13)**
O1	**96h**	**0.10003(5)**	**0.19600(5)**	**0.28204(5)**	**0.9957(21)**	**1.003(10)**

Table S10. Structural Refinement 260 K LLZO-Al0.17. R_{wp} = 2.857%, lattice parameter a = 12.95637(17) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S10 or in the discussion.

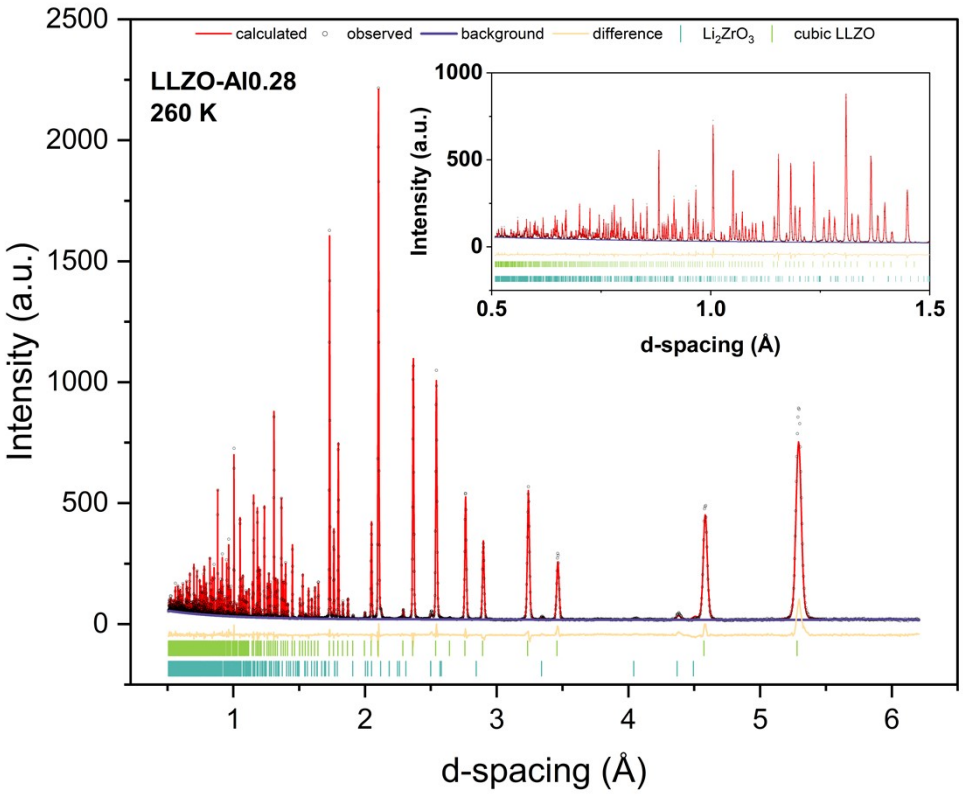


Figure S16. Rietveld refinement results and NPD for LLZO-Al0.28 at 260 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4500**	**4.97(30)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.0953**	**4.97(30)**
Li2	**96h**	**0.09748(27)**	**0.18703(31)**	**0.42464(29)**	**0.4025**	**1.25(6)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9979(19)**	**0.705(9)**
Zr1	**16a**	**0**	**0**	**0**	**0.9943(23)**	**0.576(11)**
O1	**96h**	**0.09991(4)**	**0.19622(5)**	**0.28199(4)**	**0.9971(18)**	**1.049(9)**

Table S11. Structural Refinement 260 K LLZO-Al0.28. R_{wp} = 4.088%, lattice parameter a = 12.95594(11) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S11 or in the discussion.

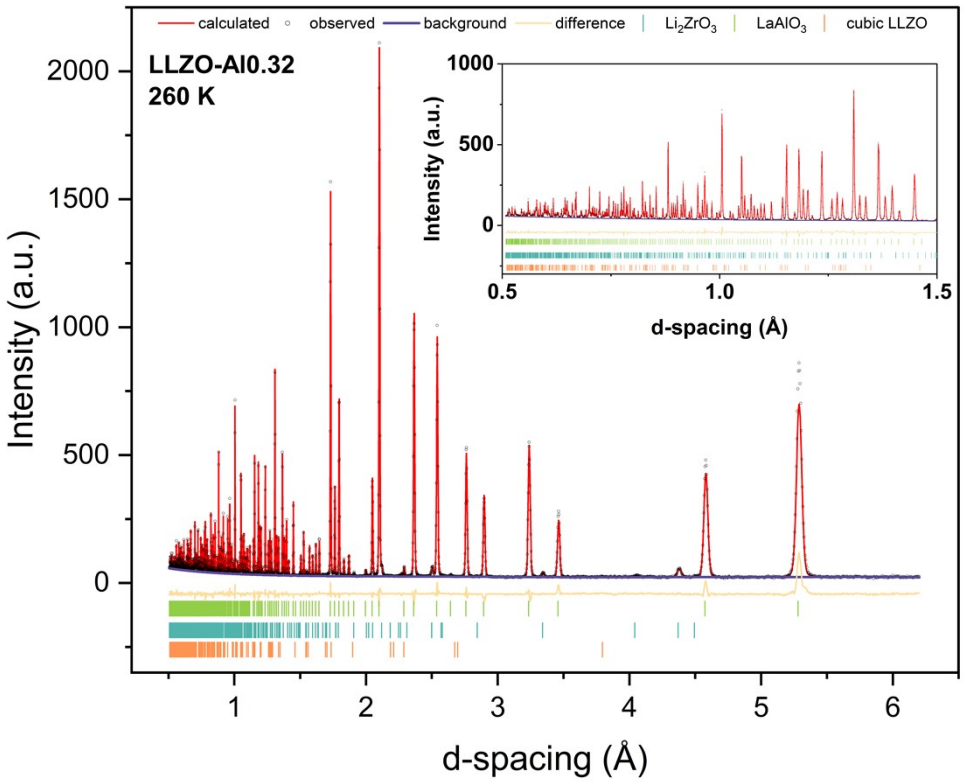


Figure S17. Rietveld refinement results and NPD for LLZO-Al0.32 at 260 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4250**	**4.5(3)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.1077**	**4.5(3)**
Li2	**96h**	**0.09777(24)**	**0.18690(27)**	**0.42460(26)**	**0.3880**	**1.11(7)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9978(17)**	**0.611(8)**
Zr1	**16a**	**0**	**0**	**0**	**0.9952(20)**	**0.474(9)**
O1	**96h**	**0.09985(4)**	**0.19626(4)**	**0.28197(3)**	**0.9966(16)**	**0.949(7)**

Table S12. Structural Refinement 260 K LLZO-Al0.32. R_{wp} = 3.743%, lattice parameter a = 12.953283(23) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S12 or in the discussion.

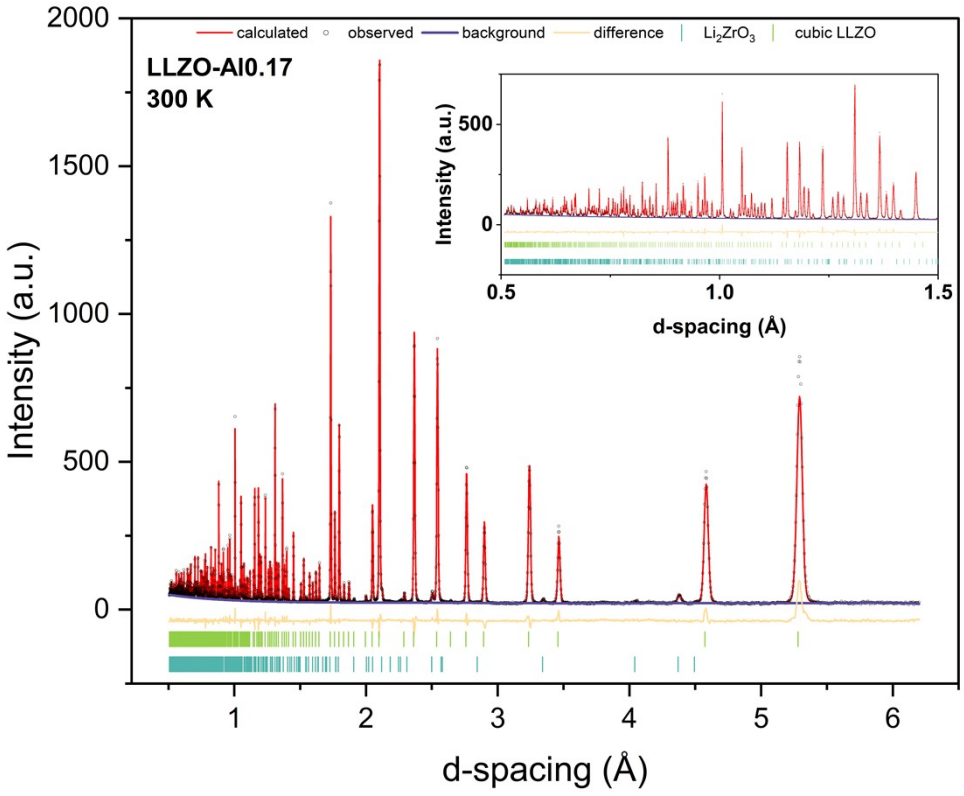


Figure S18. Rietveld refinement results and NPD for LLZO-Al0.17 at 300 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	24d	0.375	0	0.25	0.4500	3.04(17)
Al1	24d	0.375	0	0.25	0.0570	3.04(17)
Li2	96h	0.09729(25)	0.18712(29)	0.42476(28)	0.4233	1.18(7)
La1	24c	0.125	0	0.25	0.9989(19)	0.720(9)
Zr1	16a	0	0	0	0.9950(22)	0.592(11)
O1	96h	0.10002(4)	0.19607(5)	0.28195(4)	0.9945(18)	1.038(9)

Table S13. Structural Refinement 300 K LLZO-Al0.17. R_{wp} = 4.102%, lattice parameter a = 12.96027(4) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S13 or in the discussion.

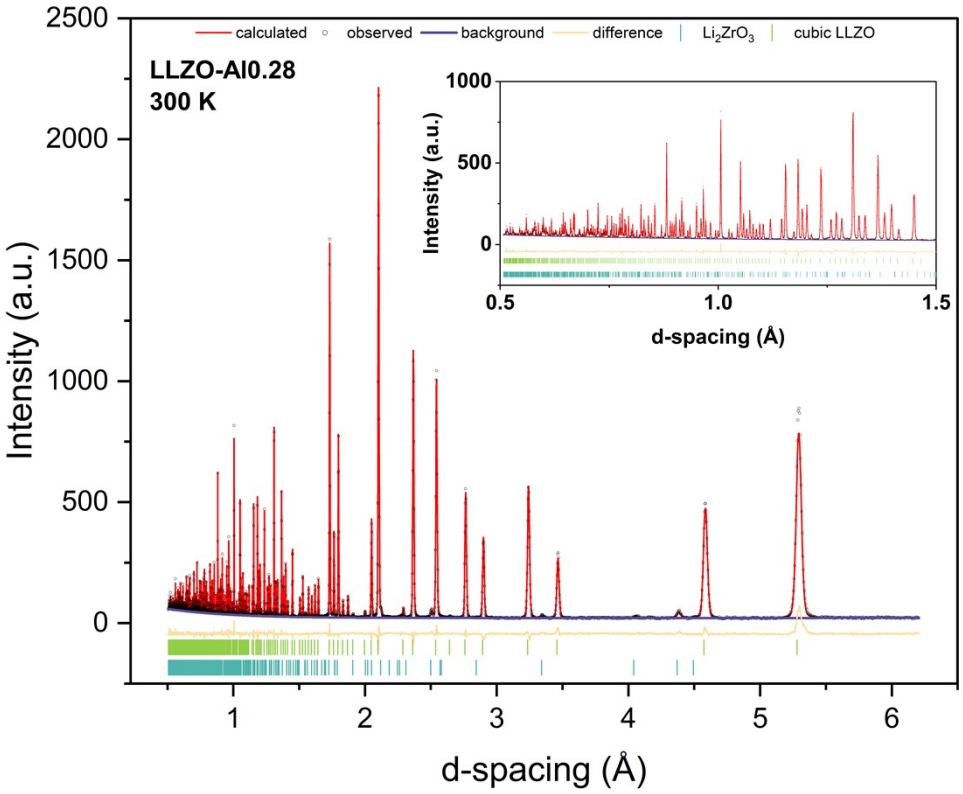


Figure S19. Rietveld refinement results and NPD for LLZO-Al0.28 at 300 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4500**	**5.4(3)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.0953**	**5.4(3)**
Li2	**96h**	**0.09732(27)**	**0.18722(31)**	**0.42480(29)**	**0.4025**	**1.40(7)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9984(18)**	**0.766(9)**

Zr1	**16a**	**0**	**0**	**0**	**0.9948(21)**	**0.650(11)**
O1	**96h**	**0.09996(4)**	**0.19627(4)**	**0.28198(4)**	**0.9976(17)**	**1.119(8)**

Table S14. Structural Refinement 300 K LLZO-Al0.28. R_{wp} = 3.956%, lattice parameter a = 12.95997(6) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S14 or in the discussion.

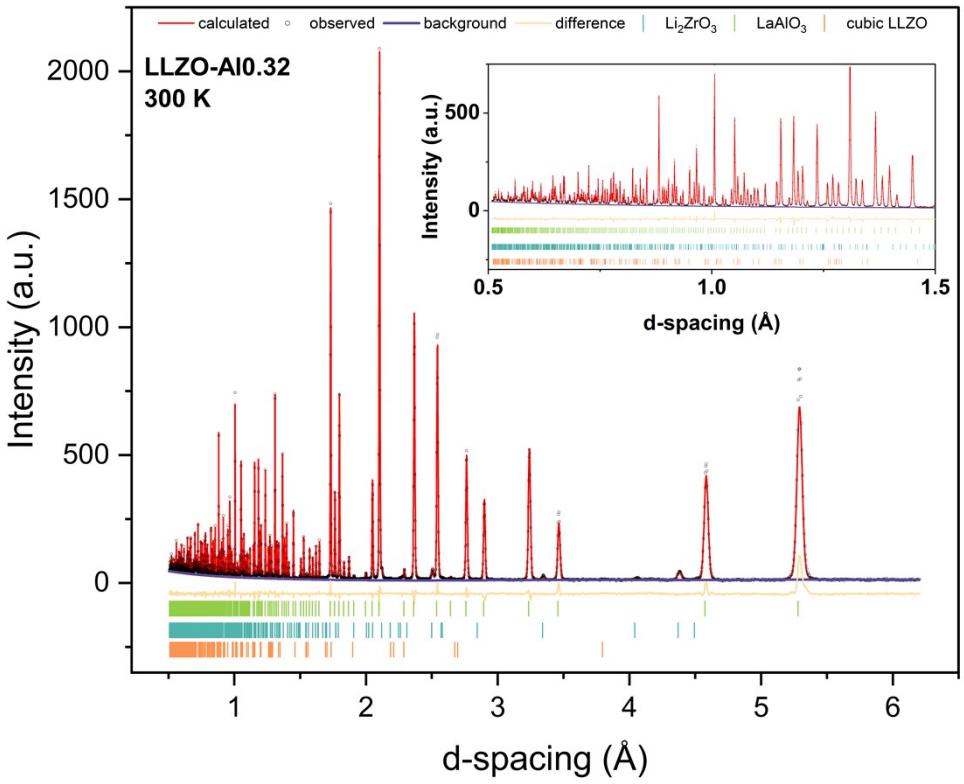


Figure S20. Rietveld refinement results and NPD for LLZO-Al0.32 at 300 K.

Element	Wyckoff Position	x	y	z	Fraction	100*U_{iso}
Li1	**24d**	**0.375**	**0**	**0.25**	**0.4250**	**4.9(3)**
Al1	**24d**	**0.375**	**0**	**0.25**	**0.1077**	**4.9(3)**

Li2	**96h**	**0.09780(24)**	**0.18682(27)**	**0.42440(26)**	**0.3880**	**1.23(6)**
La1	**24c**	**0.125**	**0**	**0.25**	**0.9973(16)**	**0.646(7)**
Zr1	**16a**	**0**	**0**	**0**	**0.9952(19)**	**0.511(9)**
O1	**96h**	**0.09993(4)**	**0.19626(4)**	**0.28195(3)**	**0.9987(15)**	**1.013(7)**

Table S15. Structural Refinement 300 K LLZO-Al0.32. R_{wp} = 4.107%, lattice parameter a = 12.95858(6) Å. Since the Li1 and Li2 fractions were manually input and defined by the minimum R_{wp} their errors are not included in Table S15 or in the discussion.

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