Supporting Information:

Wet-environment-induced structural alterations in single- and poly-crystalline LLZTO solid electrolytes studied by diffraction techniques

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Table S1. Experimental details and refinement results of neutron diffraction data between 2.5 K and 400 K for the CZ-LLZTO single crystal; for all structures: M_r = 932.8, Cubic, $Ia\bar{3}d$, Z = 8. Experiments were carried out with neutron radiation, λ = 0.793 Å using a Huber Eulerian Cradle. Refinement was on 32 parameters with 2 restraints.

	CZ-LLZTO_T=2.5K	CZ-LLZTO_T=200K	CZ-LLZTO_T=300K	CZ-LLZTO_T=400K
		Crystal data		
Temperature (K)	2.5	200	300	400
a (Å)	12.8511 (2)	12.8592 (2)	12.8775 (2)	12.9051 (2)
V (Å^3)	2122.37 (10)	2126.39 (10)	2135.48 (10)	2149.24 (10)
μ (mm^{-1})	0.04	0.03	0.03	0.03
Crystal size (mm)	2.35 × 2.15 × 1.95	2.35 × 2.15 × 1.95	2.35 × 2.15 × 1.95	2.35 × 2.15 × 1.95
		Data collection		
Absorption correction	–	–	–	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	624, 347, 289	676, 404, 289	674, 401, 291	645, 408, 267
R_{int}	0.044	0.043	0.028	0.043
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.811	0.810	0.809	0.811
		Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.038, 0.98	0.027, 0.041, 0.97	0.026, 0.033, 1.01	0.046, 0.065, 1.35
No. of reflections	347	404	401	408
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, −0.40	0.59, −0.64	0.39, −0.49	0.99, −0.97

Computer programs: Bruker *APEX2* (Bruker, 2012), *SHELXL2014*/7 (Sheldrick, 2014), *SHELXL* (Sheldrick, 2015), *ORTEP* for Windows (Farrugia, 2012), *WinGX* publication routines (Farrugia, 2012).

Table S2. Selected bond lengths for nominal $Li_6La_3ZrTaO_{12}$, as determined from the CZ-single crystal using neutron diffraction data

CZ-LLZTO_T=2.5K			
La1—O1^{i}	2.4906 (5)	Li2—O1^{vi}	1.858 (6)
La1—O1	2.5869 (5)	Li2—O1^{vii}	2.086 (5)
Zr1—O1^{ii}	2.0431 (4)	Li2—O1^{viii}	2.280 (5)
Li1—Li2^{iii}	1.628 (6)	Li2—Li1^{ix}	2.319 (6)
Li1—O1^{iv}	1.9170 (5)	Li2—O1^{x}	2.654 (5)
Li1—Li2^{v}	2.319 (6)	Li2—O1^{xi}	2.675 (5)
Li2—Li2^{vi}	0.722 (11)		
CZ-LLZTO_T=200K			
La1—O1^{i}	2.4916 (5)	Li2—O1^{vi}	1.856 (6)
La1—O1	2.5901 (5)	Li2—O1^{vii}	2.092 (5)
Zr1—O1^{ii}	2.0429 (5)	Li2—O1^{viii}	2.284 (6)
Li1—Li2^{iii}	1.631 (6)	Li2—Li1^{ix}	2.318 (6)
Li1—O1^{iv}	1.9185 (5)	Li2—O1^{x}	2.657 (6)
Li1—Li2^{v}	2.318 (6)	Li2—O1^{xi}	2.670 (5)
Li2—Li2^{vi}	0.715 (11)		
CZ-LLZTO_T=300K			
La1—O1^{i}	2.4945 (5)	Li2—O1^{vi}	1.851 (6)
La1—O1^{vi}	2.5940 (5)	Li2—O1^{vii}	2.097 (5)
Zr1—O1^{ii}	2.0446 (5)	Li2—O1^{viii}	2.297 (5)
Li1—Li2^{iii}	1.634 (6)	Li2—Li1^{ix}	2.322 (6)
Li1—O1^{iv}	1.9224 (4)	Li2—O1^{x}	2.671 (5)
Li1—Li2^{v}	2.322 (6)	Li2—O1^{xi}	2.672 (5)
Li2—Li2^{vi}	0.715 (10)		
CZ-LLZTO_T=400K			
La1—O1^{i}	2.4991 (9)	Li2—O1^{vi}	1.879 (14)
La1—O1^{xii}	2.6002 (9)	Li2—O1^{vii}	2.112 (10)
Zr1—O1^{ii}	2.0459 (9)	Li2—Li1^{ix}	2.296 (14)
Li1—Li2^{iii}	1.668 (15)	Li2—O1^{viii}	2.316 (12)
Li1—O1^{iv}	1.9291 (9)	Li2—O1^{x}	2.653 (13)
Li1—Li2^{v}	2.296 (14)	Li2—O1^{xi}	2.661 (10)
Li2—Li2^{vi}	2)		

Table S3. Lattice parameters of nominal $Li_6La_3ZrTaO_{12}$, treated in different media for different times. Estimated standard deviation is < 0.0005 Å

aging in dry air[§]		aging in distilled water		aging in glacial acetic acid	
time (h)	a (Å)				
0	12.8813	0.01	12.8845	1	12.8858
0	12.8845	0.5	12.8887	1	12.8847
48	12.8964	1	12.8886	2	12.8851
120	12.9015	2	12.8871	4	12.8920
144	12.9022	3.5	12.8888	15	12.8937
216	12.9064	6	12.8896	50	12.8969
384	12.9101	16	12.8899	88	12.8980
576	12.9141	24	12.8915	117	12.8993
912	12.9201	46	12.8935	141	12.8998
984	12.9211	67	12.8948	186	12.9010
1368	12.9254	88	12.8959	190	12.9012
1656	12.9279	111	12.8962	310	12.9028
1800	12.9284	163	12.8976	449	12.9048
2232	12.9311	185	12.8977	549	12.9077
2712	12.9329	231	12.8989	735	12.9092
3504	12.9364	352	12.9004	1023	12.9120
3960	12.9381	399	12.9018	1167	12.9137
4776	12.9411	497	12.9031	1298	12.9141
4896	12.9406	552	12.9039	1958	12.9174
5592	12.9425	870	12.9081	6264	12.9289
6456	12.9434	1044	12.9093		
6888	12.9431				
8376	12.9455				
8760	12.9454				
10680	12.9483				

aging in humid air[$]		aging in distilled water (stirring)		mild hydrothermal conditions[&]	
time (h)	a (Å)	time (h)	a (Å)	time (h)	a (Å)
0.1	12.8900	17	12.8959	0.1	12.8813
48	12.9019	18	12.8970	24	12.9399
192	12.9134	24	12.8985	48	12.9575
432	12.9259	67	12.9007	72	12.9615
1104	12.9403	168	12.9028	168	12.9774
1128	12.9404	233	12.9040	336	12.9826
1440	12.9430	528	12.9093		
		636	12.9108		
		741	12.9121		

§ 25°C, relative humidity 15 – 20 %, $ 25°C saturated water vapor

Table S4. Experimental details and refinement results of single crystal X-ray diffraction data for the CZ-LLZTO and S-LLZTO single crystal in the pristine state and aged in acetic acid (Acet) and H_2O for different times (given in days in the sample ID); for all structures: Cubic, $Ia\bar{3}d$, $Z = 8$. Experiments were carried out at 293 K with Mo $K\alpha$ radiation using a SMART APEX. Absorption was corrected for by multi-scan methods, multi-scan correction with *APEX2* software (Bruker 2012), H^+ content as calculated from the difference in Li^+ content in pristine and aged samples.

	CZ-LLZTO_pristine	CZ-LLZTO_H_2O_32d	CZ-LLZTO_Acet_32d	S-LLZTO_pristine	S-LLZTO_Acet_14d
			Crystal data		
Chemical formula	$Li_{5.28}La_{2.92}Ta_{1.09}Zr_{0.91}O_{12}$	$Li_{4.33}H_{0.95}La_{2.95}O_{12}Ta_{1.09}Zr_{0.91}$	$Li_{4.54}H_{0.74}La_{2.95}Ta_{1.12}Zr_{0.88}O_{12}$	$La_{2.89}Li_{5.34}Ta_{0.94}Zr_{1.06}O_{12}$	$Li_{4.44}H_{0.90}La_{2.91}Ta_{0.94}Zr_{1.06}O_{12}$
M_r	914.49	915.77	919.78	897.31	897.96
a (Å)	12.8768 (2)	12.8951 (5)	12.8974 (9)	12.8757 (9)	12.9041 (2)
V (Å^3)	2135.13 (10)	2144.2 (2)	2145.4 (4)	2134.6 (4)	2148.74 (10)
μ (mm^{-1})	23.48	23.43	23.77	21.98	22.13
Crystal size (mm)	0.14 × 0.13 × 0.07	0.08 × 0.08 × 0.07	0.15 × 0.14 × 0.08	0.08 × 0.08 × 0.07	0.14 × 0.13 × 0.08
			Data collection		
T_{min}, T_{max}	0.06, 0.20	0.576, 0.747	0.576, 0.747	0.576, 0.747	0.576, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31473, 523, 509	31513, 444, 442	30642, 446, 444	32066, 446, 434	32365, 440, 385
R_{int}	0.047	0.053	0.028	0.028	0.045
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.884	0.835	0.837	0.838	0.829
			Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.038, 1.49	0.022, 0.048, 1.45	0.02, 0.040, 1.46	0.016, 0.030, 1.39	0.013, 0.025, 1.31
No. of reflections	523	444	446	446	440
No. of parameters	27	31	32	27	30
No. of restraints	1	2	2	1	2
H-atom treatment	–	Only H-atom coordinates refined	All H-atom parameters refined	–	Only H-atom coordinates refined
	$w = 1/[\sigma^2(F_o^2) + 25.2759P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + 59.1181P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + 45.2335P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0047P)^2 + 17.9709P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0067P)^2 + 6.2165P]$ where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.71, −0.81	1.04, −0.91	0.92, −0.76	0.58, −0.52	0.45, −0.61

Table S5. Selected bond lengths (Å) for pristine and aged nominal $Li_6La_3ZrTaO_{12}$ single crystals, as determined from X-ray diffraction for the data collections given in Table S4.

CZ-LLZTO_pristine			
La1—O1^{i}	2.492 (2)	Li2—O1^{vii}	1.88 (2)
La1—O1^{ii}	2.591 (2)	Li2—O1^{viii}	2.15 (2)
Zr1—O1^{iii}	2.047 (2)	Li2—O1^{ix}	2.28 (2)
Li1—Li2^{iv}	1.68 (2)	Li2—O1^{x}	2.62 (2)
Li1—O1^{v}	1.924 (2)	Li2—O1^{xi}	2.62 (2)
Li1—Li2^{vi}	2.27 (2)		
CZ-LLZTO_H2O_32d			
La1—O1^{i}	2.495 (3)	Li2—O1^{vii}	1.89 (3)
La1—O1^{vii}	2.593 (3)	Li2—O1^{viii}	2.16 (3)
Zr1—O1^{iii}	2.049 (3)	Li2—O1^{ix}	2.30 (3)
Li1—Li2^{iv}	1.70 (3)	Li2—O1^{x}	2.61 (3)
Li1—O1^{vi}	1.928 (3)	Li2—O1^{xi}	2.62 (3)
Li1—Li2^{v}	2.26 (3)		
CZ-LLZTO_ACET_32d			
La1—O1^{xii}	2.496 (3)	Li2—O1^{vii}	1.89 (3)
La1—O1^{vii}	2.595 (3)	Li2—O1^{viii}	2.15 (3)
Zr1—O1^{iii}	2.049 (3)	Li2—O1^{ix}	2.29 (3)
Li1—Li2^{iv}	1.69 (2)	Li2—O1^{x}	2.61 (2)
Li1—O1^{vi}	1.927 (3)	Li2—O1^{xi}	2.63 (2)
Li1—Li2^{v}	2.27 (2)		
S-LLZTO_pristine			
La1—O1^{i}	2.4924 (19)	Li2—O1^{vii}	1.878 (17)
La1—O1	2.5891 (19)	Li2—O1^{viii}	2.113 (16)
Zr1—O1^{xiii}	2.0514 (18)	Li2—O1^{ix}	2.280 (16)
Li1—Li2^{xiv}	1.657 (15)	Li2—O1^{x}	2.627 (16)
Li1—O1^{v}	1.9201 (19)	Li2—O1^{xi}	2.659 (16)
Li1—Li2^{vi}	2.296 (15)		
S-LLZTO_Acet_14d			
La1—O1^{xii}	2.4991 (18)	Li2—O1^{vii}	1.868 (14)
La1—O1	2.5961 (16)	Li2—O1^{viii}	2.117 (14)
Zr1—O1^{xv}	2.0523 (16)	Li2—O1^{ix}	2.276 (13)
Li1—Li2^{iv}	1.641 (13)	Li2—O1^{x}	2.651 (13)
Li1—O1^{vi}	1.9260 (16)	Li2—O1^{xi}	2.668 (13)
Li1—Li2^{v}	2.319 (13)		

Symmetry code(s): (i) $-z+1/4, -y+1/4, -x+1/4$; (ii) $x, -y, -z+1/2$; (iii) $x-1/4, z-1/4, y-1/4$; (iv) $-y+1/2, z-1/2, x$; (v) $-z+3/4, y-1/4, -x+1/4$; (vi) $-z+3/4, -y+1/4, x+1/4$; (vii) $-x+1/4, z-1/4, y+1/4$; (viii) $-y+1/2, -z+1/2, -x+1/2$; (ix) $y, -z+1/2, x+1/2$; (x) $-y+1/4, x+1/4, -z+3/4$; (xi) $y-1/4, -x+1/4, -z+3/4$; (xii) z, x, y; (xiii) $-x+1/4, -z+1/4, -y+1/4$; (xiv) $y+1/4, -x+1/4, z-1/4$; (xv) $z-1/4, y-1/4, x-1/4$.

Table S6: Experimental details and refinement results of single crystal X-ray diffraction data for the CZ-LLZTO and S-LLZTO single crystals, aged under hydrothermal conditions at 363 K for different times (given in days in the sample ID); for all structures: Cubic, $I\bar{4}3d$, $Z = 8$. Experiments were carried out at 293 K with Mo $K\alpha$ radiation using a SMART APEX. Absorption was corrected for by multi-scan methods, multiscan correction with *APEX2* software (Bruker 2012). Only H-atom coordinates were refined. The absolute structure was obtained using Refined as an inversion twin.

	CZ_LLZTO_363k_1d	CZ-LLZO_363K_5d	CZ-LLZTO_363K_7d	CZ_LLZTO_363K_14d	S-LLZTO_363K_14d
			Crystal data		
Chemical formula	$La_{2.95}Li_{3.73}H_{1.57}Ta_{1.10}Zr_{0.90}O_{12}$	$La_{2.95}Li_{3.29}H_{2.91}Ta_{1.10}Zr_{0.90}O_{12}$	$La_{2.92}Li_{3.04}H_{2.26}Ta_{1.05}Zr_{0.95}O_{12}$	$La_{2.95}Li_{2.71}H_{2.59}Ta_{1.09}Zr_{0.91}O_{12}$	$La_{2.95}Li_{2.86}H_{2.47}Ta_{0.99}Zr_{1.01}O_{12}$
M_r	913.03	909.13	897.82	903.18	895.81
a (Å)	12.9466 (3)	12.9667 (8)	12.9768 (3)	12.9834 (2)	12.9839 (2)
V (Å^3)	2170.04 (15)	2180.2 (4)	2185.26 (15)	2188.59 (10)	2188.85 (10)
μ (mm^{-1})	23.35	23.19	22.57	23.02	22.13
Crystal shape	Plate	Box-shaped	Plate	Box-shaped	Isometric
Crystal size (mm)	0.14 × 0.13 × 0.07	0.08 × 0.08 × 0.07	0.14 × 0.12 × 0.08	0.13 × 0.12 × 0.09	0.07 × 0.07 × 0.06
			Data collection		
T_{min}, T_{max}	0.065, 0.210	0.195, 0.205	0.055, 0.175	0.075, 0.145	0.225, 0.272
No. of measured, independent and observed [I > 2σ(I)] reflections	33706, 888, 885	33201, 890, 886	34144, 889, 883	34330, 891, 886	34887, 895, 867
R_{int}	0.053	0.052	0.042	0.038	0.032
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.835	0.836	0.834	0.835	0.835
			Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.033, 1.19	0.016, 0.033, 1.20	0.016, 0.032, 1.31	0.015, 0.030, 1.23	0.015, 0.034, 1.08
No. of reflections	888	890	889	891	895
No. of parameters	50	50	49	48	48
No. of restraints	8	7	8	8	2
	$w = 1/[\sigma^2(F_o^2) + 17.6898P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + 17.9485P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + 15.3802P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0029P)^2 + 14.9255P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0152P)^2 + 10.299P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.92, −0.74	0.95, −0.61	0.91, −0.67	0.74, −0.74	0.78, −0.95
Absolute structure parameter	0.58 (6)	0.46 (6)	0.47 (5)	0.50 (4)	4)

Table S7: Selected bond lengths (Å) for hydrothermally aged nominal $Li_6La_3ZrTaO_{12}$ single crystals, as determined from X-ray diffraction for the data collections given in Table S6.

CZ_LLZTO_363k_1d			
La1—O1^{i}	2.508 (3)	Li1—O1^{i}	1.966 (3)
La1—O2^{ii}	2.517 (4)	Li1—Li3^{i}	2.19 (6)
La1—O1	2.562 (3)	Li2—Li3^{vii}	1.79 (6)
La1—O2^{i}	2.600 (4)	Li2—O2^{viii}	1.947 (4)
Zr1—O1^{iii}	1.929 (4)	Li3—O2^{i}	1.95 (6)
Zr1—O2^{iv}	2.186 (4)	Li3—O2^{ix}	2.18 (6)
Ta1—O1^{v}	2.044 (3)	Li3—O2^{x}	2.38 (6)
Ta1—O2^{ii}	2.059 (3)	Li3—O1^{xi}	2.53 (6)
O1—H1	0.72 (12)	Li3—O1^{x}	2.65 (6)
Li1—O1^{vi}	1.966 (3)		
CZ-LLZO_363K_5d			
La1—O1^{i}	2.511 (3)	Li1—O1^{vi}	1.967 (3)
La1—O2^{ii}	2.522 (4)	Li1—Li3^{i}	2.16 (5)
La1—O1	2.567 (3)	Li2—Li3^{vii}	1.82 (5)
La1—O2^{i}	2.602 (4)	Li2—O2^{viii}	1.952 (4)
Zr1—O1^{v}	1.936 (4)	Li3—O2^{i}	1.96 (5)
Zr1—O2^{iv}	2.183 (4)	Li3—O2^{ix}	2.21 (5)
Ta1—O1^{v}	2.047 (3)	Li3—O2^{x}	2.40 (5)
Ta1—O2^{ii}	2.062 (3)	Li3—O1^{xi}	2.52 (5)
O1—H1	0.73 (13)	Li3—O1^{x}	2.63 (5)
CZ-LLZTO_363K_7d			
La1—O1^{i}	2.512 (3)	O1—H1	0.93 (13)
La1—O2^{ii}	2.525 (4)	Li1—Li3^{i}	1.82 (7)
La1—O1^{xii}	2.566 (3)	Li1—O1^{vi}	1.971 (3)
La1—O2^{i}	2.605 (4)	Li1—O1^{i}	1.971 (3)
Zr1—O1^{iii}	1.928 (4)	Li2—O2^{viii}	1.953 (4)
Zr1—O2^{iv}	2.198 (4)	Li2—Li3^{vii}	2.16 (7)
Ta1—O1^{v}	2.053 (3)	Li3—O2^{i}	2.01 (7)
Ta1—O2^{ii}	2.061 (4)		
CZ_LLZTO_363K_14d			
La1—O1^{i}	2.511 (3)	Li1—O1^{vi}	1.978 (3)
La1—O2^{ii}	2.531 (3)	Li1—Li3^{i}	2.16 (17)
La1—O1^{xii}	2.557 (3)	Li2—Li3^{vii}	1.83 (17)
La1—O2^{i}	2.602 (3)	Li2—O2^{viii}	1.962 (3)
Zr1—O1^{iii}	1.933 (3)	Li3—O2^{i}	1.96 (17)
Zr1—O2^{iv}	2.190 (4)	Li3—O2^{ix}	2.20 (16)
Ta1—O1^{v}	2.029 (3)	Li3—O2^{x}	2.45 (16)
Ta1—O2^{ii}	2.083 (3)	Li3—O1^{xi}	2.53 (16)
O1—H1	0.73 (11)	Li3—O1^{x}	2.66 (16)
S-LLZTO_363K_2d			
La1—O1^{i}	2.507 (4)	Li1—O1^{vi}	1.955 (3)
La1—O2^{ii}	2.517 (4)	Li1—Li3^{i}	2.18 (4)
La1—O1	2.574 (4)	Li2—Li3^{vii}	1.79 (4)
La1—O2^{i}	2.595 (4)	Li2—O2^{viii}	1.943 (4)
Zr1—O1^{iii}	1.941 (6)	Li3—O2^{i}	1.93 (4)
Zr1—O2^{iv}	2.191 (7)	Li3—O2^{ix}	2.22 (4)
Ta1—O2^{ii}	2.051 (5)	Li3—O2^{x}	2.37 (4)
Ta1—O1^{v}	2.069 (5)	Li3—O1^{xi}	2.54 (4)
O1—H1	0.69 (14)	Li3—O1^{x}	2.61 (4)
S-LLZTO_363K_14d			
La1—O1^{i}	2.509 (3)	Li1—O1^{vi}	1.976 (3)
La1—O2^{ii}	2.532 (3)	Li1—Li3^{i}	2.15 (14)
La1—O1	2.554 (3)	Li2—Li3^{vii}	1.83 (14)
La1—O2^{i}	2.599 (3)	Li2—O2^{viii}	1.961 (3)

Zr1—O1^{iii}	1.934 (7)	Li3—O2^{i}	1.92 (14)
Zr1—O2^{iv}	2.202 (8)	Li3—O2^{ix}	2.27 (14)
Ta1—O1^{v}	2.045 (5)	Li3—O2^{x}	2.40 (13)
Ta1—O2^{ii}	2.077 (5)	Li3—O1^{xi}	2.51 (13)
O1—H1	0.63 (12)	Li3—O1^{x}	2.60 (14)

Symmetry code(s): (i) *z*, *x*, *y*; (ii) −*x*, −*y*+1/2, *z*; (iii) *x*−1/4, *z*−1/4, *y*−1/4; (iv) *z*, −*x*, −*y*+1/2; (v) *z*−1/4, *y*−1/4, *x*−1/4; (vi) −*z*+3/4, −*y*+1/4, *x*+1/4; (vii) *y*+3/4, −*x*+1/4, −*z*+3/4; (viii) *x*+3/4, −*z*+1/4, −*y*+3/4; (ix) −*y*+3/4, −*x*+1/4, *z*+1/4; (x) *y*−1/4, −*x*+1/4, −*z*+3/4; (xi) −*y*+1/4, *x*+1/4, −*z*+3/4; (xii) *x*, −*y*, −*z*+1/2.

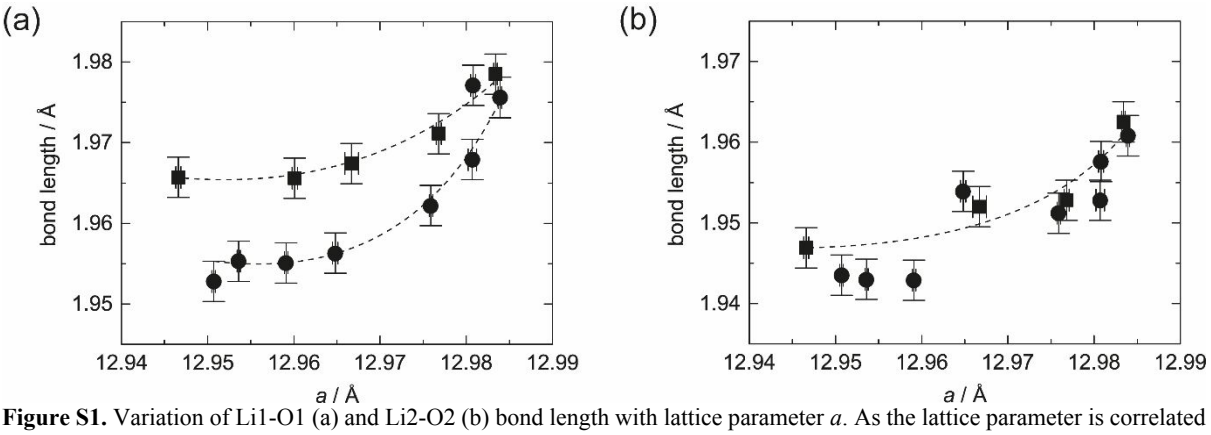

Figure S1. Variation of Li1-O1 (a) and Li2-O2 (b) bond length with lattice parameter *a*. As the lattice parameter is correlated with the Li^+/H^+ exchange, but H^+ cannot be determined quantitatively, and Li^+ content determination also is affected by larger uncertainties, it is chosen to plot bond lengths vs. lattice parameters. Note that CZ-LLZTO and S-LLZTO depict some different values but show almost the same behaviour for the Li1-O1 bond length.

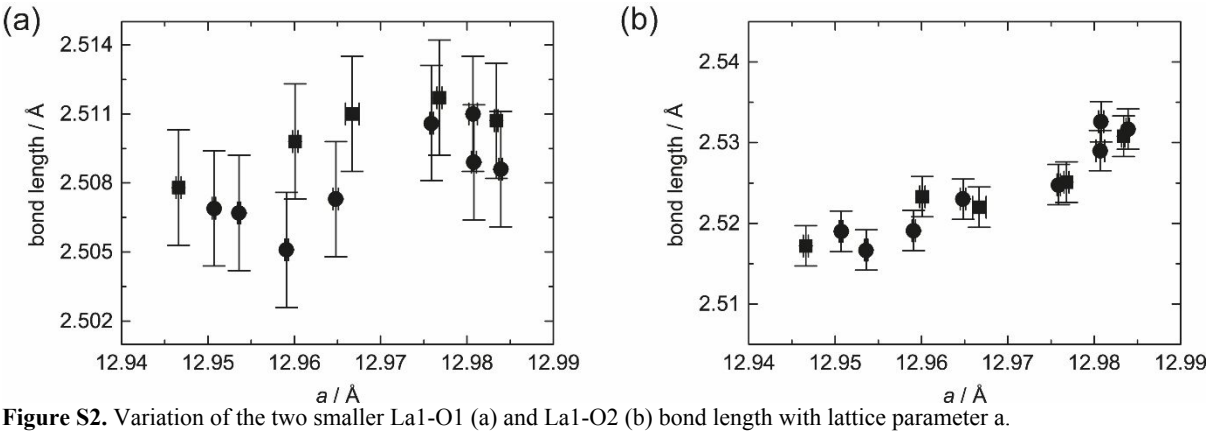

Figure S2. Variation of the two smaller La1-O1 (a) and La1-O2 (b) bond length with lattice parameter a.

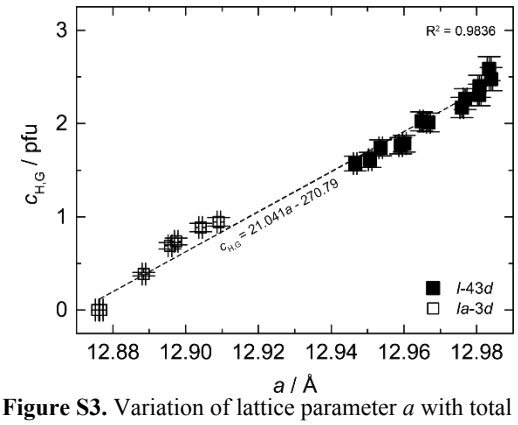

Figure S3. Variation of lattice parameter *a* with total H^+ content.

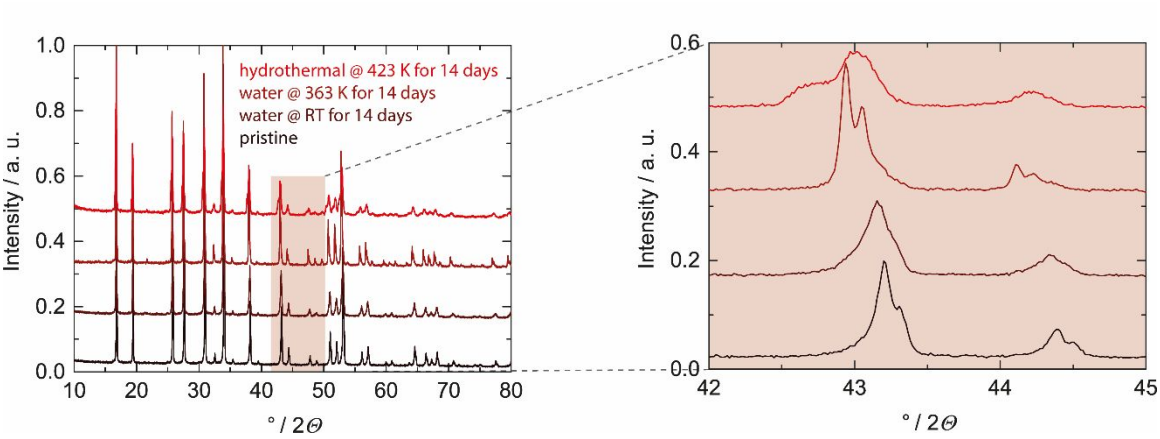

Figure S4. Powder XRD pattern of S-LLZTO before and after aging in water at RT for 14 days, water at 367 K for 14 days, and water at 423 K for 14 days under hydrothermal conditions.