Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information to

Garnet to hydrogarnet: Effect of post synthesis treatment on cation substituted LLZO solid electrolyte and its effect on Li ion conductivity

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Table 1: Substituting and substituted cations for aliovalent substitution in LLZO: Ionic radii[1] and coordination in binary oxides, cn = coordination number.

Ion	**Radii / Å**		**Coordination in binary oxide**
	Tetrahedral (IV), based on halides	**Octahedral (VI)**, based on halides	
Li^{+}	0.59	0.76	-
Al^{3+}	0.39 (**V**: 0.48)	0.535	corundum: octahedral[2]
Fe^{3+}	0.49	Low spin: 0.55 High spin: 0.645	octahedral
Ga^{3+}	0.47	0.62	octahedral
Zr^{4+}	0.59	0.72	25°C: Baddeleyite, cn=7 >1100°C cn=8[2]
Nb^{5+}	0.48	0.64	NbO: Nb_6-Clusters[2] Nb_2O_5: distorted octahedra[3]
Ta^{5+}	-	0.64	Ta_2O_5 cn=7[4]/ cn=6 distorted octahedra[5]
W^{6+}	0.42	0.6	Octahedral in WO_3[2]
La^{3+}	VI: 1.032 XII: 1.36		Octahedral with one additional oxygen, cn= 7[6]

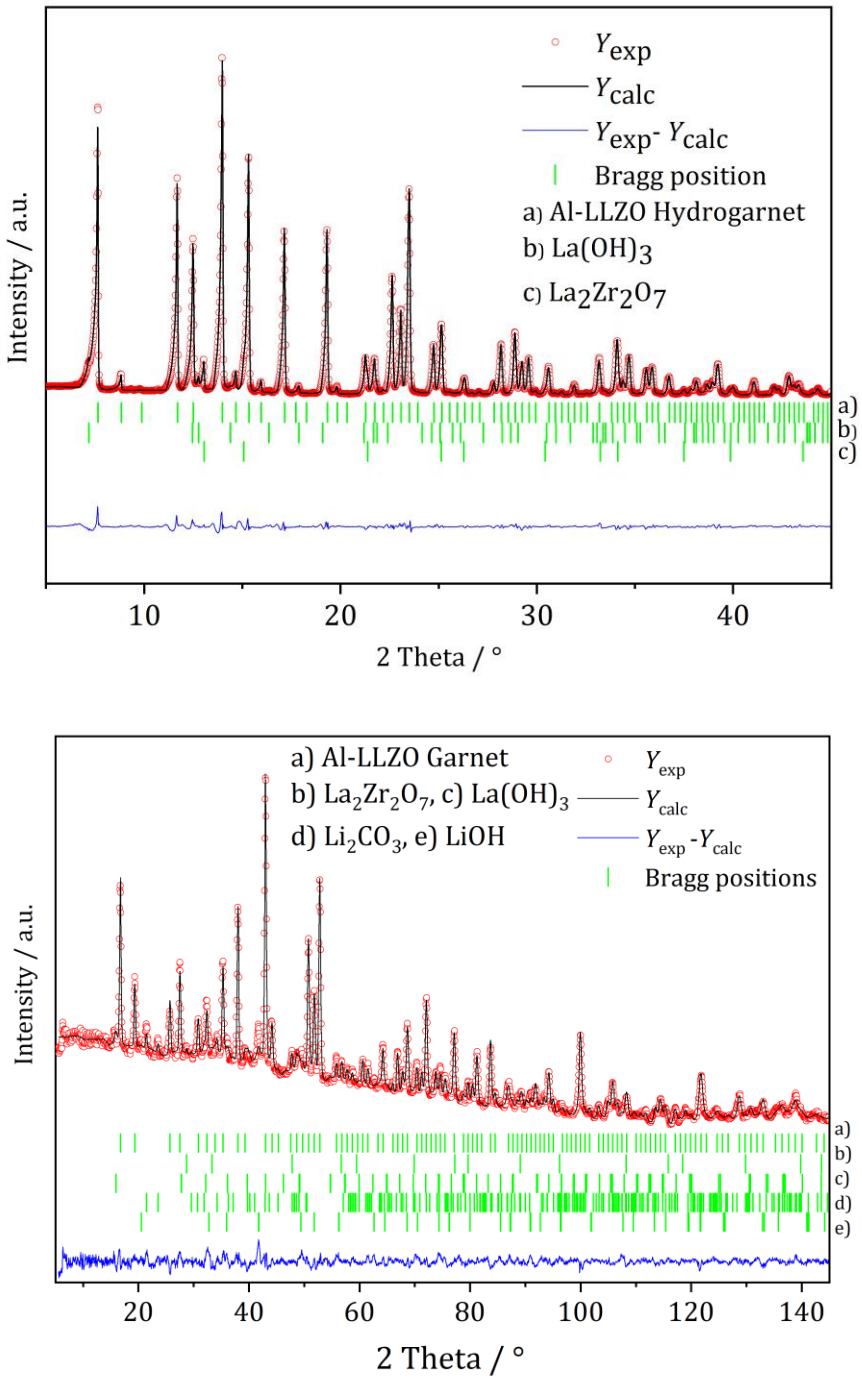

Figure S1: Rietveld co-refinement against, top: X-ray diffraction pattern (Mo $K_{\alpha 1}$) and bottom: Neutron diffraction pattern (λ = 1.5482 Å) of commercial Al-substituted LLZO.

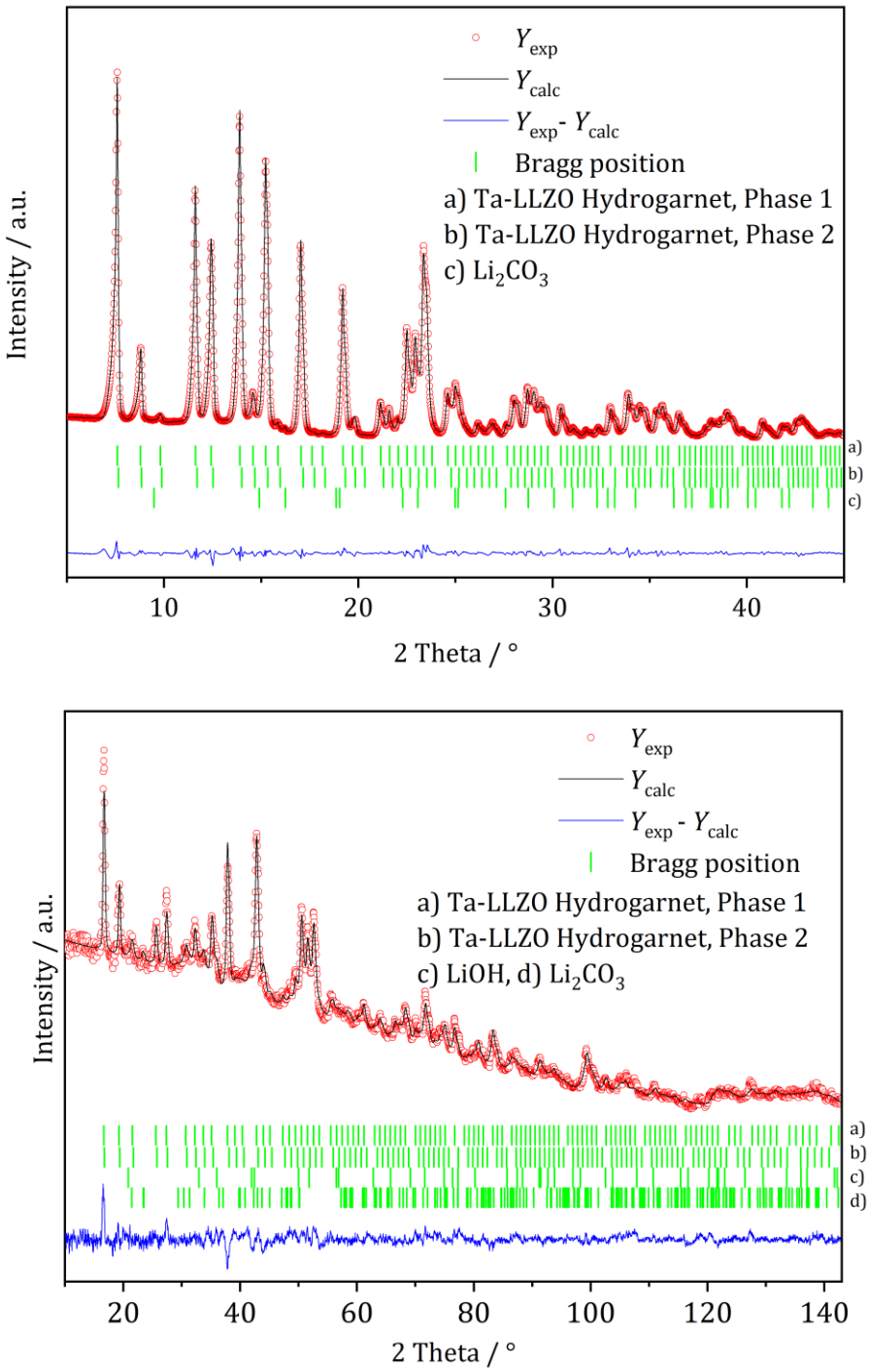

Figure S2: Rietveld co-refinement against, top: X-ray diffraction pattern (Mo K_{a1}) and bottom: Neutron diffraction pattern (λ = 1.5482 Å) of commercial Ta-substituted LLZO

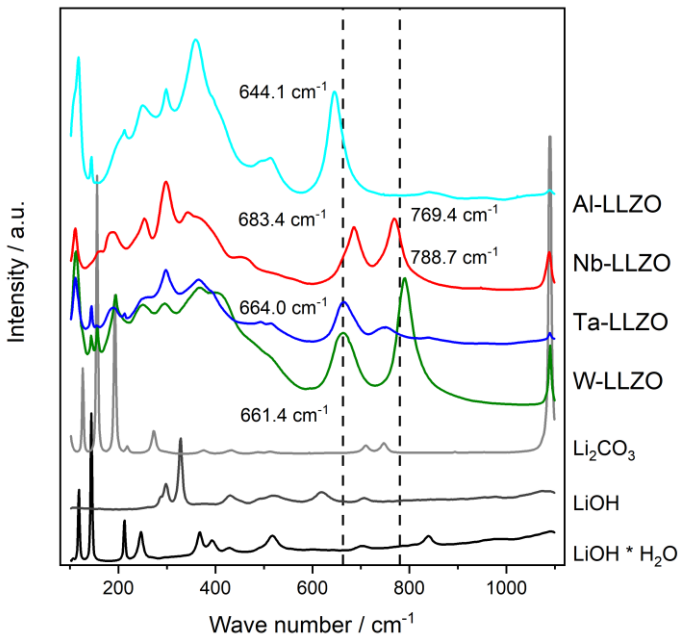

Figure S3: Raman spectra of Al-, Nb-, Ta- and W-substituted LLZO, LiOH, LiOHH_2O, and Li_2CO_3.*

Table S2: Results of the ICP-OES analysis, n.a.: not analyzed.

Atom	%	Al-LLZO		Nb-LLZO		Ta-LLZO		W-LLZO	
		Mean	±	Mean	±	Mean	±	Mean	±
Li	(wt-%)	4.39	0.09	4.76	0.10	4.26	0.09	5.14	0.11
C	(wt-%)	0.956	0.083	1.30	0.11	2.52	0.22	0.620	0.054
O	(wt-%)	27.9	2.2	28.6	2.3	27.0	2.1	22.9	1.8
Al	(wt-%)	0.632	0.016	n.a.	-	n.a.	-	n.a.	-
Zr	(wt-%)	19.5	0.4	12.7	0.3	12.8	0.3	15.7	0.3
Nb	(wt-%)	n.a.	-	5.78	0.01	n.a.	-	n.a.	-
La	(wt-%)	45.6	-	42.3	-	39.3	-	43.4	-
Ta	(wt-%)	n.a.	-	n.a.	-	8.70	0.01	n.a.	-
W	(wt-%)	n.a.	-	n.a.	-	n.a.	-	6.79	0.23
Sum	(wt-%)	98.98		95.44		94.58		94.55	
Li	(Atom-%)	21.5		23.0		22.1		27.5	
C	(Atom-%)	-		-		-		-	
O	(Atom-%)	59.3		60.0		60.9		53.1	
Al	(Atom-%)	0.796		-		-		-	
Zr	(Atom-%)	7.27		4.67		5.06		6.39	
Nb	(Atom-%)	-		2.09		-		-	

La	(Atom-%)	11.2		10.2		10.2		11.6	
Ta	(Atom-%)	-		-		1.73		-	
W	(Atom-%)	-		-		-		1.37	
Sum	(Atom-%)	100.00		100.00		100.00		100.00	

Table S3: Results of the Rietveld refinement of synthesized Al-, Nb- Ta-, and W-substituted LLZO.

Substituent: Stoichiometry	Crystal structure	Lattice parameter *a* / Å	Cell volume / Å^3	Structural strain [d*d*/*d* *10^{-4}]
Al: $Li_{6.1}Al_{0.3}La_3Zr_2O_{12}$	Garnet	13.002	2198.040	20.87
Nb: $Li_{6.5}La_3Zr_{1.5}Nb_{0.5}O_{12}$	Garnet	12.959	2176.422	30.61
$Li_{6.625}La_3Zr_{1.625}Ta_{0.375}O_{12}$	Hydrogarnet	13.007	2200.520	31.16
W: $Li_{6.4}La_3Zr_{1.7}W_{0.3}O_{12}$	Garnet	12.926	2159.894	18.08

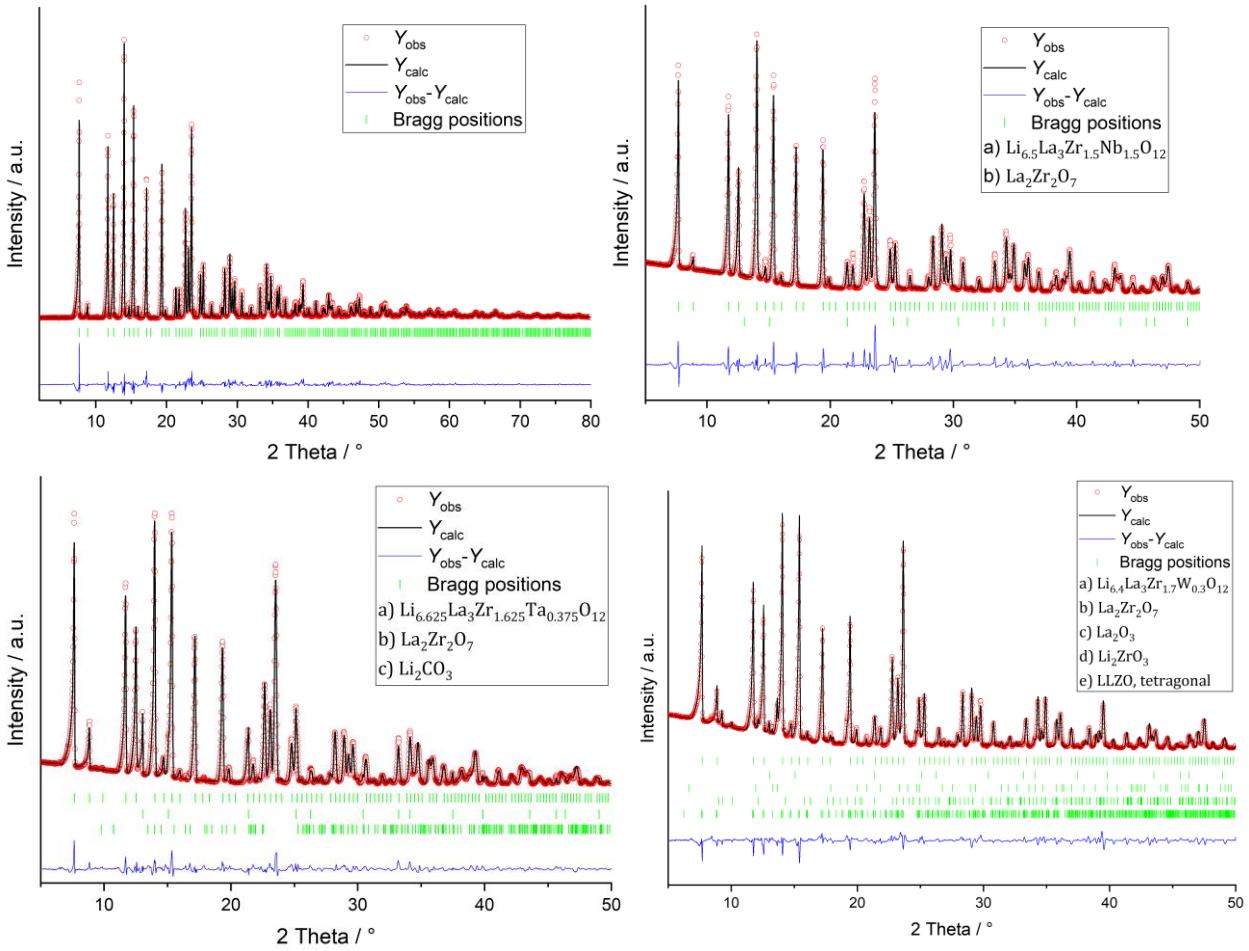

Figure S4: Rietveld refinement based on diffraction patterns (Mo $K_{\alpha 1}$) of synthesized Al-, Nb-, Ta-, and W-substituted LLZO.

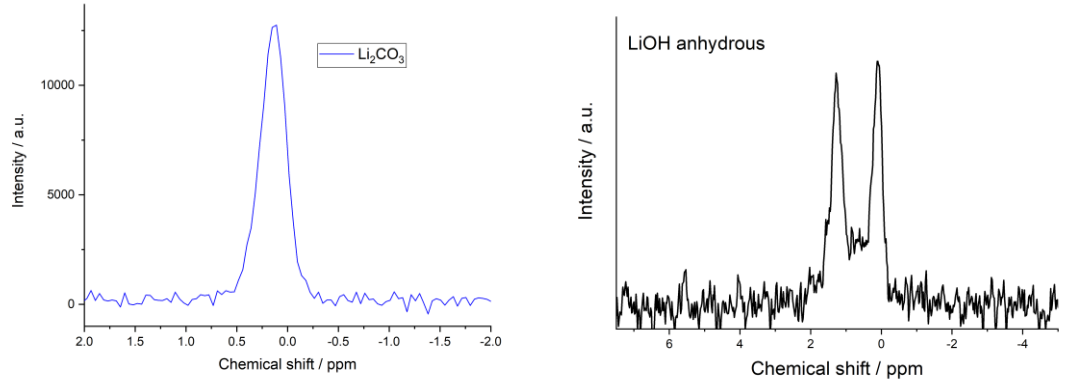

Figure S5: Left: ^{7}Li MAS NMR spectrum of Li_2CO_3 and right: ^{6}Li MAS NMR spectrum of dried and anhydrous LiOH.

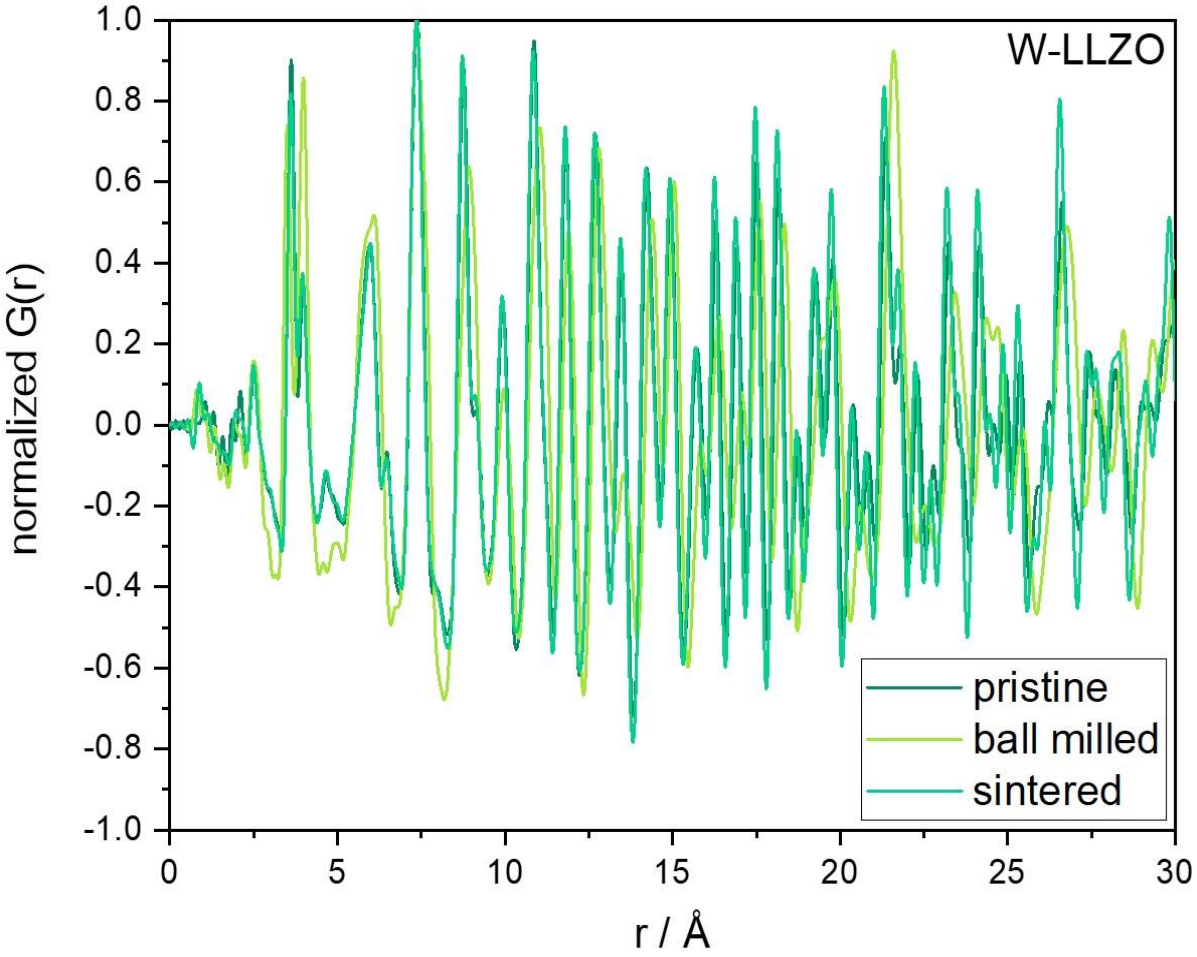

Figure S6: normalized (by max) pair distribution function of pristine, ball milled and sintered W-LLZO. Note that the lowered intensity of PDF peaks at higher r in the pristine PDF is due to a higher dampening factor (Qdamp).

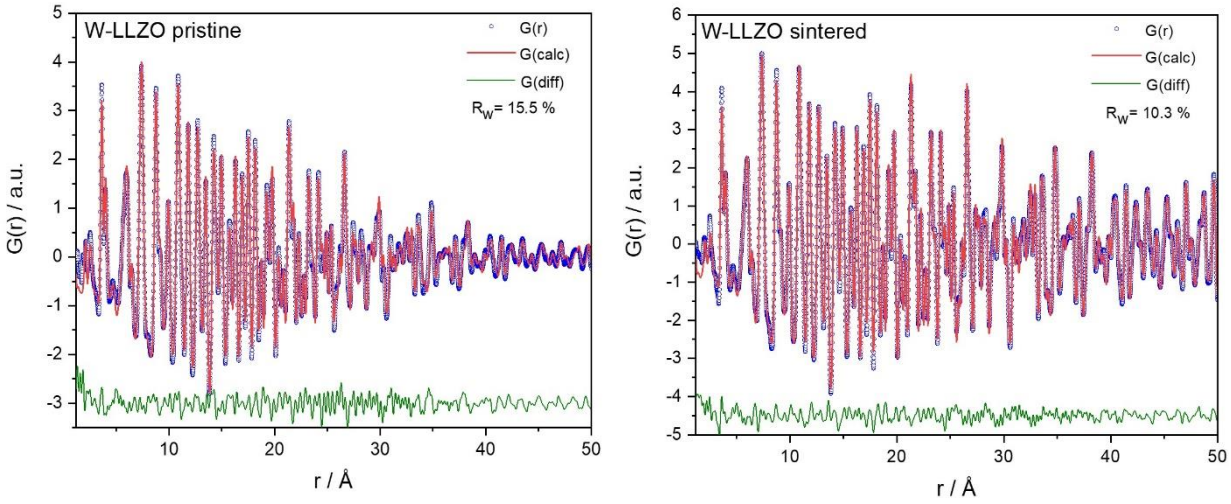

Figure S7: Real space Rietveld refinement based on PDFs of pristine and sintered W-substituted LLZO.

Summaries of real space Rietveld small box fits using PDFgui:

PDF Fit Summary pristine W-LLZO

```
================================================================================
 PDF REFINEMENT
   Using PDFFIT version : 1.1
 ================================================================================
 --------------------------------------------------------------------------------
 PHASE 1 : 20200305_cf_w-llzo_mse
 --------------------------------------------------------------------------------
 Scale factor          : 0.411362 (0.01)
   Particle diameter    : not applied
   Step cutoff          : not applied
 Quad. corr. factor     : 0
 Lin. corr. factor      : 1.68761
 Low r sigma ratio      : 1
 R cutoff [A]           : 0
 Lattice parameters     :12.9587 (0.0017)    12.9587 (0.0017)    12.9587 (0.0017)
         & angles     :90                90                90
DATA SET : 1 (string)
 --------------------------------------------------------------------------------
 Data range in r [A]    : 1.19     -> 50          Step dr  : 0.01
 Calculated range       : 1.19     -> 51.3906
 Refinement r range     : 1.19     -> 50          Data pts : 0     -> 4881
 Reduced chi squared    : 0.0227414
```

Rw - value : 0.154591

Experimental settings :
Radiation : X-Rays
Termination at Qmax : 27.11 A**-1
DQ dampening Qdamp : 0.0468316 (0.0011) A**-1
DQ broadening Qbroad : not applied
Scale factor : 1

Selected phases and atoms for this data set :
Phase 1 :
Atoms (i) : LA ZR W LI O
Atoms (j) : LA ZR W LI O

Relative phase content in terms of

	atoms	unit cells	mass
Phase 1 :	1	1	1

PARAMETER INFORMATION :

Number of constraints : 1110
Number of refined parameters : 10
Number of fixed parameters : 1

Refinement parameters :
1:12.9587 (0.0017) 2:0.411362 (0.01) 3:1.68761
6:0.0468316 (0.0011) 14:0.0108977 (0.00064) 15:0.00918106 (0.00076)
16:0.0170382 (0.018) 17:0.0408885 (0.0076) 21:0.0999987 (0.0016)
22:0.202442 (0.0022) 23:0.280528 (0.0023)

REFINEMENT INFORMATION:

Number of iterations : 5
Reduced chi squared : 0.0227414
Rw - value : 0.154591

Correlations greater than 0.8 :

*** none ***
==========

PDF Fit Summary ball milled W-LLZO

```
================================================================================
 PDF REFINEMENT
Using PDFFIT version : 1.1
 ================================================================================
 --------------------------------------------------------------------------------
 PHASE 1 : 220_W_LLZO
 --------------------------------------------------------------------------------
 Scale factor          : 0.400113 (0.011)
   Particle diameter    : not applied
   Step cutoff          : not applied
 Quad. corr. factor     : 0
 Lin. corr. factor      : 1.68
 Low r sigma ratio      : 1
 R cutoff [A]           : 0
 Lattice parameters     :13.0381 (0.0024)    13.0381 (0.0024)    13.0381 (0.0024)
         & angles     :90                90                90

 DATA SET : 1 (string)
 --------------------------------------------------------------------------------
 Data range in r [A]    : 1.19     -> 40          Step dr  : 0.01
 Calculated range       : 1.19     -> 41.5425
 Refinement r range     : 1.19     -> 40          Data pts : 0     -> 3881
 Reduced chi squared    : 0.030492
 Rw - value             : 0.189065

 Experimental settings  :
   Radiation            : X-Rays
   Termination at Qmax  : 24.44 A**-1
   DQ dampening Qdamp   : 0.02 A**-1
   DQ broadening Qbroad : not applied
   Scale factor         : 1

 Selected phases and atoms for this data set :
   Phase 1 :
     Atoms (i) :  LA  ZR  W  LI  O
     Atoms (j) :  LA  ZR  W  LI  O

 Relative phase content in terms of
         atoms                unit cells            mass
 Phase 1 :1                    1                    1

 --------------------------------------------------------------------------------
```

PARAMETER INFORMATION :

Number of constraints : 1253
Number of refined parameters : 17
Number of fixed parameters : 1

Refinement parameters :
1:13.0381 (0.0024) 2:0.400113 (0.011) 3:1.68
15:0.013892 (0.0021) 16:3.19792 (1.8) 17:0.0443428 (0.011)
21:0.131876 (0.0007) 261:0.0104125 (0.00038) 1781:0.112816 (0.0043)
1782:0.188424 (0.0054) 1783:0.280637 (0.0048) 2261:0.953836 (0.005)
2262:0.344739 (0.0031) 2263:0.978239 (0.0054) 2274:0.0132193 (0.0036)
2275:0.0233563 (0.0039) 2276:0.0109719 (0.003) 2279:0.00776589 (0.002)

REFINEMENT INFORMATION:

Number of iterations : 5
Reduced chi squared : 0.030492
Rw - value : 0.189065

Correlations greater than 0.8 :

*** none ***

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PDF Fit Summary of sintered W-LLZO

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PDF REFINEMENT
Using PDFFIT version : 1.1

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PHASE 1 : UNNAMED

Scale factor : 0.492705 (0.0085)
Particle diameter : not applied
Step cutoff : not applied
Quad. corr. factor : 0
Lin. corr. factor : 1.31527
Low r sigma ratio : 1
R cutoff [A] : 0
Lattice parameters :12.9311 (0.00083) 12.9311 (0.00083) 12.9311 (0.00083)

& angles :90 90 90

DATA SET : 1 (string)

Data range in r [A] : 1.19 -> 50 Step dr : 0.01
Calculated range : 1.19 -> 51.5559
Refinement r range : 1.19 -> 50 Data pts : 0 -> 4881
Reduced chi squared : 0.0234903
Rw - value : 0.103677

Experimental settings :
Radiation : X-Rays
Termination at Qmax : 24.23 A**-1
DQ dampening Qdamp : 0.0298057 (0.00064) A**-1
DQ broadening Qbroad : not applied
Scale factor : 1

Selected phases and atoms for this data set :
Phase 1 :
Atoms (i) : LA ZR W LI O
Atoms (j) : LA ZR W LI O

Relative phase content in terms of
atoms unit cells mass
Phase 1 :1 1 1

PARAMETER INFORMATION :

Number of constraints : 1110
Number of refined parameters : 10
Number of fixed parameters : 1

Refinement parameters :
1:12.9311 (0.00083) 2:0.492705 (0.0085) 3:1.31527
6:0.0298057 (0.00064) 14:0.00997342 (0.00032) 15:0.00867781 (0.00042)
16:0.0252504 (0.015) 17:0.0368109 (0.0047) 21:0.102233 (0.0015)
22:0.20137 (0.0017) 23:0.27939 (0.0016)

REFINEMENT INFORMATION:

Number of iterations : 6
Reduced chi squared : 0.0234903

Rw - value : 0.103677

Correlations greater than 0.8 :

*** none ***

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Comparison of crystal structures of the same symmetry *Ia*-3*d* (No. 230)

Structure #1 pristine W-LLZO

```
230
12.95870 12.95870 12.95870 90.00000 90.00000 90.00000
5
La     1       24c     0.125000        0.000000        0.250000
Zr     1       16a     0.000000        0.000000        0.000000
Li     1       24d     0.375000        0.000000        0.250000
Li     2       96h     0.431000        0.144000        0.172000
O      1       96h     0.100000        0.202440        0.280530
```

Structure #2 sintered W-LLZO

```
230
12.93110 12.93110 12.93110 90.00000 90.00000 90.00000
5
La     1       24c     0.125000        0.000000        0.250000
Zr     1       16a     0.000000        0.000000        0.000000
Li     1       24d     0.375000        0.000000        0.250000
Li     2       96h     0.431000        0.144000        0.172000
O      1       96h     0.102230        0.201370        0.279390
```

Description of Structure #2 in the most similar configuration to Structure #1

```
230
12.931100 12.931100 12.931100 90.000000 90.000000 90.000000
5
La     1       24c     0.125000        0.000000        0.250000
Zr     1       16a     0.000000        0.000000        0.000000
Li     1       24d     0.375000        0.000000        0.250000
Li     2       96h     0.431000        0.144000        0.172000
O      1       96h     0.102230        0.201370        0.279390
```

Transformation matrix (**P**, p): **a,b,c** ; 0,0,0
Matrix form:

$$(\mathbf{P}, p) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

Atom pairings and distances

Atom Mappings					
WP		**Atom**	**Coordinates in S_1**	**Atom**	**Coordinates in S_2**
24c	(1/8,0,1/4)	La1	(0.125000,0.000000,0.250000)	La1	(0.125000,0.000000,0.250000)
16a	(0,0,0)	Zr1	(0.000000,0.000000,0.000000)	Zr1	(0.000000,0.000000,0.000000)
24d	(3/8,0,1/4)	Li1	(0.375000,0.000000,0.250000)	Li1	(0.375000,0.000000,0.250000)
96h	(x,y,z)	Li2	(0.431000,0.144000,0.172000)	Li2	(0.431000,0.144000,0.172000)
96h	(x,y,z)	O1	(0.100000,0.202440,0.280530)	O1	(0.102230,0.201370,0.279390)

WP		**Atom**	**Atomic Displacements**			
			u_x	**u_y**	**u_z**	**$\|u\|$**
24c	(1/8,0,1/4)	La1	0.0000	0.0000	0.0000	0.0000
16a	(0,0,0)	Zr1	0.0000	0.0000	0.0000	0.0000

24d	(3/8,0,1/4)	Li1	0.0000	0.0000	0.0000	0.0000
96h	(x,y,z)	Li2	0.0000	0.0000	0.0000	0.0000
96h	(x,y,z)	O1	0.0022	-0.0011	-0.0011	0.0353

NOTE: u_x, u_y and u_z are given in relative units. |u| is the absolute distance given in Å

Evaluation of the structure similarity

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0012	0.0353	0.0132	0.001

- Lattice and atomic position criteria:
    - The degree of lattice distortion (**S**) is the spontaneous strain (sum of the squared eigenvalues of the strain tensor divided by 3). For the given two structures, the **degree of lattice distortion (S)** is **0.0012**.
    - The maximum distance (**$d_{max.}$**) shows the maximal displacement between the atomic positions of the paired atoms. The **maximum distance ($d_{max.}$)** in this case is: **0.0353 Å**
- The arithmetic mean (**d_{av}**) of the distance. In this case, the **arithmetic mean (d_{av})** is **0.0132 Å**
.
- The measure of similarity (**Δ**) (Bergerhoff *et al.*, 1998) is a function of the differences in atomic positions (weighted by the multiplicities of the sites) and the ratios of the corresponding lattice parameters of the structures. The **measure of similarity (Δ)** calculated for this case is **0.001**.

Comparison of crystal structures of the same symmetry *I*-43*d* (No. 220)

Structure #1 hydrogarnet W-LLZO (r = 50 Å)

```
220
13.03710 13.03710 13.03710 90.00000 90.00000 90.00000
8
```

La	1	24d	0.131560	0.000000	0.250000
Zr	1	16c	0.010540	0.010540	0.010540
Li	1	12a	0.375000	0.000000	0.250000
Li	2	12b	0.875000	0.000000	0.250000
Li	3	48e	0.396390	0.195550	0.083330
Li	4	48e	0.945550	0.646390	0.166670
O	1	48e	0.108650	0.198960	0.285820
O	2	48e	0.444910	0.849510	0.479940

Structure #2 hydrogarnet W-LLZO (r = 6.5 Å)

220

13.04560 13.04560 13.04560 90.00000 90.00000 90.00000

8

La	1	24d	0.131800	0.000000	0.250000
Zr	1	16c	0.010700	0.010700	0.010700
Li	1	12a	0.375000	0.000000	0.250000
Li	2	12b	0.875000	0.000000	0.250000
Li	3	48e	0.396390	0.195550	0.083330
Li	4	48e	0.945550	0.646390	0.166670
O	1	48e	0.114210	0.189550	0.271240
O	2	48e	0.455580	0.850640	0.473200

Description of Structure #2 in the most similar configuration to Structure #1

220

13.045600 13.045600 13.045600 90.000000 90.000000 90.000000

8

La	1	24d	0.131800	0.000000	0.250000
Zr	1	16c	0.010700	0.010700	0.010700

Li	1	12a	0.375000	0.000000	0.250000
Li	2	12b	0.875000	0.000000	0.250000
Li	3	48e	0.396390	0.195550	0.083330
Li	4	48e	0.945550	0.646390	0.166670
O	1	48e	0.114210	0.189550	0.271240
O	2	48e	0.455580	0.850640	0.473200

Transformation matrix (**P**, p): **a,b,c** ; 0,0,0
Matrix form:

$$(\mathbf{P}, p) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

Atom pairings and distances

Atom Mappings					
WP		**Atom**	**Coordinates in S_1**	**Atom**	**Coordinates in S_2**
24d	(x,0,1/4)	La1	(0.131560,0.000000,0.250000)	La1	(0.131800,0.000000,0.250000)
16c	(x,x,x)	Zr1	(0.010540,0.010540,0.010540)	Zr1	(0.010700,0.010700,0.010700)
12a	(3/8,0,1/4)	Li1	(0.375000,0.000000,0.250000)	Li1	(0.375000,0.000000,0.250000)
12b	(7/8,0,1/4)	Li2	(0.875000,0.000000,0.250000)	Li2	(0.875000,0.000000,0.250000)
48e	(x,y,z)	Li3	(0.396390,0.195550,0.083330)	Li3	(0.396390,0.195550,0.083330)
48e	(x,y,z)	Li4	(0.945550,0.646390,0.166670)	Li4	(0.945550,0.646390,0.166670)
48e	(x,y,z)	O1	(0.108650,0.198960,0.285820)	O1	(0.114210,0.189550,0.271240)
48e	(x,y,z)	O2	(0.444910,0.849510,0.479940)	O2	(0.455580,0.850640,0.473200)

WP		**Atom**	**Atomic Displacements**			
			u_x	**u_y**	**u_z**	**$\|u\|$**
24d	(x,0,1/4)	La1	0.0002	0.0000	0.0000	0.0031
16c	(x,x,x)	Zr1	0.0002	0.0002	0.0002	0.0036
12a	(3/8,0,1/4)	Li1	0.0000	0.0000	0.0000	0.0000
12b	(7/8,0,1/4)	Li2	0.0000	0.0000	0.0000	0.0000

48e	(x,y,z)	Li3	0.0000	0.0000	0.0000	0.0000
48e	(x,y,z)	Li4	0.0000	0.0000	0.0000	0.0000
48e	(x,y,z)	O1	0.0056	-0.0094	-0.0146	0.2376
48e	(x,y,z)	O2	0.0107	0.0011	-0.0067	0.1652

NOTE: u_x, u_y and u_z are given in relative units. |u| is the absolute distance given in Å

Evaluation of the structure similarity

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0004	0.2376	0.0760	0.008

- Lattice and atomic position criteria:
    - The degree of lattice distortion (**S**) is the spontaneous strain (sum of the squared eigenvalues of the strain tensor divided by 3). For the given two structures, the **degree of lattice distortion (S)** is **0.0004**.
    - The maximum distance (**$d_{max.}$**) shows the maximal displacement between the atomic positions of the paired atoms. The **maximum distance ($d_{max.}$)** in this case is: **0.2376 Å**
- The arithmetic mean (**d_{av}**) of the distance. In this case, the **arithmetic mean (d_{av})** is **0.0760 Å**
.
- The measure of similarity (**Δ**) (Bergerhoff *et al.*, 1998) is a function of the differences in atomic positions (weighted by the multiplicities of the sites) and the ratios of the corresponding lattice parameters of the structures. The **measure of similarity (Δ)** calculated for this case is **0.008**.

Comparison of crystal structures of the different symmetries Ia-3d (No. 230) [= pristine W-LLZO) *I*-43*d* (No. 220) [= ball milled W-LLZO, r= 50 Å)

Atom pairings and distances (W was omitted in calculation, because problems with calculations occurred)

Atom Mappings

WP		Atom	Coordinates in S_1	Atom	Coordinates in S_2
24d	(x,0,1/4)	La1	(0.125000,0.000000,0.250000)	La1	(0.131560,0.000000,0.250000)
16c	(x,x,x)	Zr1	(0.000000,0.000000,0.000000)	Zr1	(0.010540,0.010540,0.010540)
12a	(3/8,0,1/4)	Li1	(0.375000,0.000000,0.250000)	Li1	(0.375000,0.000000,0.250000)
12b	(7/8,0,1/4)	Li12	(0.875000,0.000000,0.250000)	Li2	(0.875000,0.000000,0.250000)
48e	(x,y,z)	Li2	(0.431000,0.144000,0.172000)	Li3	(0.396390,0.195550,0.083330)
48e	(x,y,z)	Li22	(0.894000,0.681000,0.078000)	Li4	(0.945550,0.646390,0.166670)
48e	(x,y,z)	O1	(0.100000,0.202440,0.280530)	O1	(0.108650,0.198960,0.285820)
48e	(x,y,z)	O12	(0.452440,0.850000,0.469470)	O2	(0.444910,0.849510,0.479940)

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
24d	(x,0,1/4)	La1	-0.0066	0.0000	0.0000	0.0855
16c	(x,x,x)	Zr1	-0.0105	-0.0105	-0.0105	0.2380
12a	(3/8,0,1/4)	Li1	0.0000	0.0000	0.0000	0.0000
12b	(7/8,0,1/4)	Li12	0.0000	0.0000	0.0000	0.0000
48e	(x,y,z)	Li2	0.0346	-0.0515	0.0887	1.4112
48e	(x,y,z)	Li22	-0.0515	0.0346	-0.0887	1.4112
48e	(x,y,z)	O1	-0.0086	0.0035	-0.0053	0.1398
48e	(x,y,z)	O12	0.0075	0.0005	-0.0105	0.1683

NOTE: u_x, u_y and u_z are given in relative units. |u| is the absolute distance given in Å

Evaluation of the Global Distortion

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0035	1.4112	0.6099	0.066

- Lattice and atomic position criteria:
    - The degree of lattice distortion (S) is the spontaneous strain (sum of the squared eigenvalues of the strain tensor divided by 3). For the given two structures, the **degree of lattice distortion (S)** is **0.0035**.
    - The maximum distance ($d_{max.}$) shows the maximal displacement between the atomic positions of the paired atoms. The **maximum distance ($d_{max.}$)** in this case is: **1.4112 Å**

- The average distance (d_{av}) is defined as the average over the primitive unit cell of the distances between the atomic positions of the paired atoms. For this case the **average distance (d_{av})** is calculated as **0.6099 Å**.

- The measure of compatibility (Δ) (Bergerhoff *et al.*, 1998) is a function of the differences in atomic positions (weighted by the multiplicities of the sites) and the ratios of the corresponding lattice parameters of the structures (the comparison being between the transformed high symmetry structure into the low symmetry structure's setting and the reference low symmetry structure). The **measure of compatibility (Δ)** calculated for this case is **0.066**.

Electrochemical impedance spectra of commercial LLZO

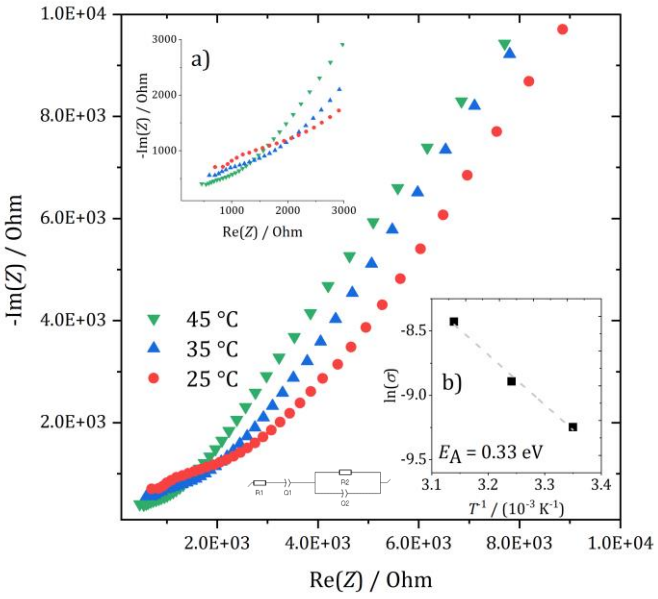

Figure S8: Nyquist Plot of impedance spectroscopy measurement of a sintered Nb-LLZO Pellet, a) Zoom, b) Arrhenius approach, dashed line shows a fit according to ***Fehler! Verweisquelle konnte nicht gefunden werden.****.*

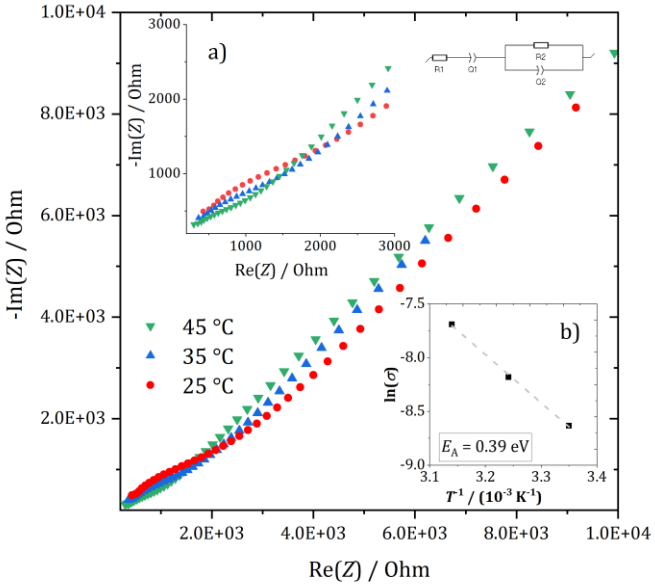

Figure S9: Nyquist Plot of impedance spectroscopy measurement of a sintered Ta-LLZO Pellet, a) Zoom, b) Arrhenius approach, dashed line shows a fit according to ***Fehler! Verweisquelle konnte nicht gefunden werden.****.*

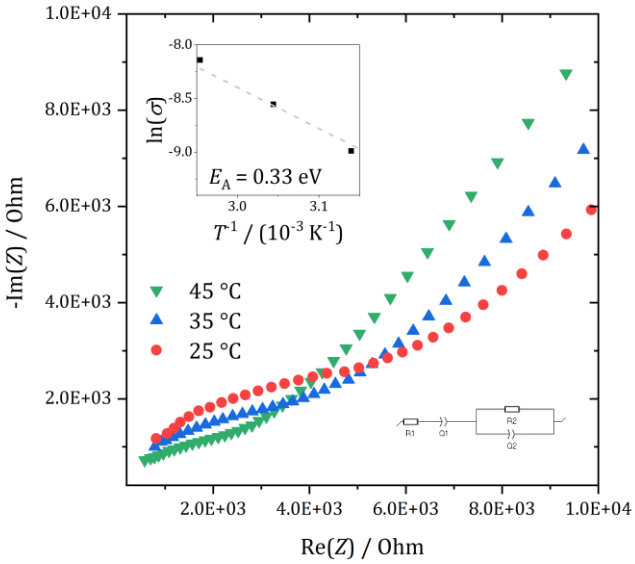

Figure S10: Nyquist Plot of impedance spectroscopy measurement of a sintered W-LLZO pellet, Inset: Arrhenius approach, dashed line shows a fit according to ***Fehler! Verweisquelle konnte nicht gefunden werden.****.*

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