

Supporting Information

The Role of Precursor Decomposition in Low-Temperature Wet-Chemical Synthesis and Crystallization of Li-Garnet Solid Electrolyte Films

Lucie Quincke¹, Gaurav Anand¹, Farheen N. Sayed^{2,3}, Clare P. Grey^{2,3}, Barbara A. J. Lechner¹,
Jennifer L.M. Rupp^{1,4,5,*}

¹Technical University of Munich, TUM School of Natural Sciences, Department of Chemistry,
Lichtenbergstr. 4, 85748 Garching, Germany

²Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2
1EW, UK

³The Faraday Institution, Harwell Science and Innovation Campus, Didcot OX11 0RA, UK

⁴TUMint. Energy Research GmbH, Lichtenbergstr. 4, Garching, Germany

⁵Fritz-Haber-Institut of the Max-Planck-Society, Faradayweg 4-6, 14195 Berlin, Germany

corresponding author: jrupp@tum.de

Table S1: ICP-OES results of LLZO films after deposition and after annealing at 750 °C. Measurements were performed on a 5800 ICP-OES from Agilent Technologies. Films were scratched off and dissolved in aqua regia before dilution for the ICP-measurements. For comparison, the obtained concentrations were normalized to the expected lanthanum content of 3.0.

	Li	Al	La	Zr
Expected	11.0	0.25	3.0	2.0
As-deposited	10.8	0.28	3.0	1.8
Annealed at 750°C	10.4	0.21	3.0	1.8

Table S2: Weight losses observed in STA analysis as shown in Figure S1 for the Al:LLZO film with a total weight of 5.7mg.

Step #	Temperature range (°C)	Weight loss (%)
1	30-175	4.1
2	230-260	0
3	175-350	6.5
4	350-445	12.4
5.1	445-540	6.0
5.2	540-650	13.7
6	650-750	1.5
Total loss		44.2

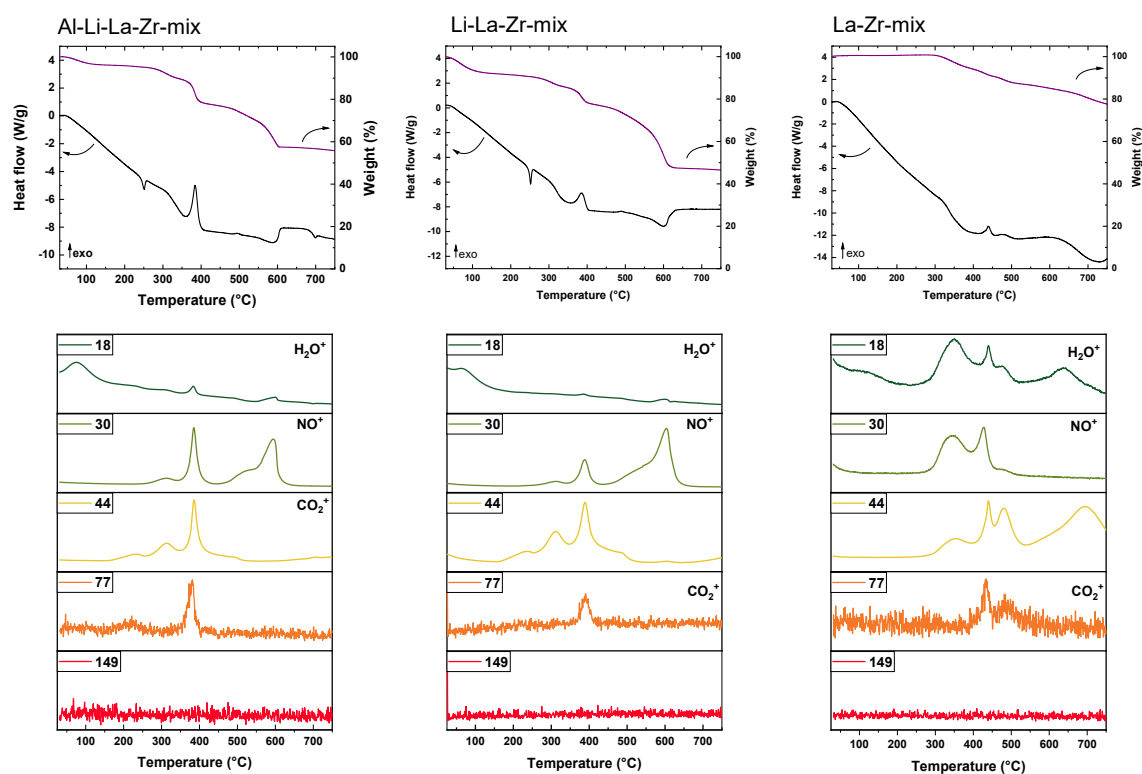


Figure S1: TGA/DSC curves of as deposited films with varying compositions and mass spectrometry of evolving gases recorded during heating to 750°C. Traces of MS fragments with a mass over charge ratio of m/z 18, 30, 44, 77 and 149 are shown exemplarily for evaporation of water, decomposition of nitrates, carbonaceous compounds, aromatics and DEHP, respectively. a) Li-garnet film (“Al-Li-La-Zr-mix”), b) Li-La-Zr-mix film and c) La-Zr-mix film.

Table S3: Weight losses observed in STA analysis as shown in Figure S1 for the Li-La-Zr-film with a total weight of 5.8mg.

Step #	Temperature range (°C)	Weight loss (%)
1	30-200	8.6
2	200-350	5.9
3	350-440	8.6
4	440-515	5.1
5	515-655	24.6
Total loss		52.8

Table S4: Weight losses observed in STA analysis as shown in Figure S1 for the La-Zr-film with a total weight of 3.9mg.

Step #	Temperature range (°C)	Weight loss (%)
1	30-395	6.2
2	395-455	3.8
3	455-540	3.7
4	540-750	9.3
Total loss		23.0

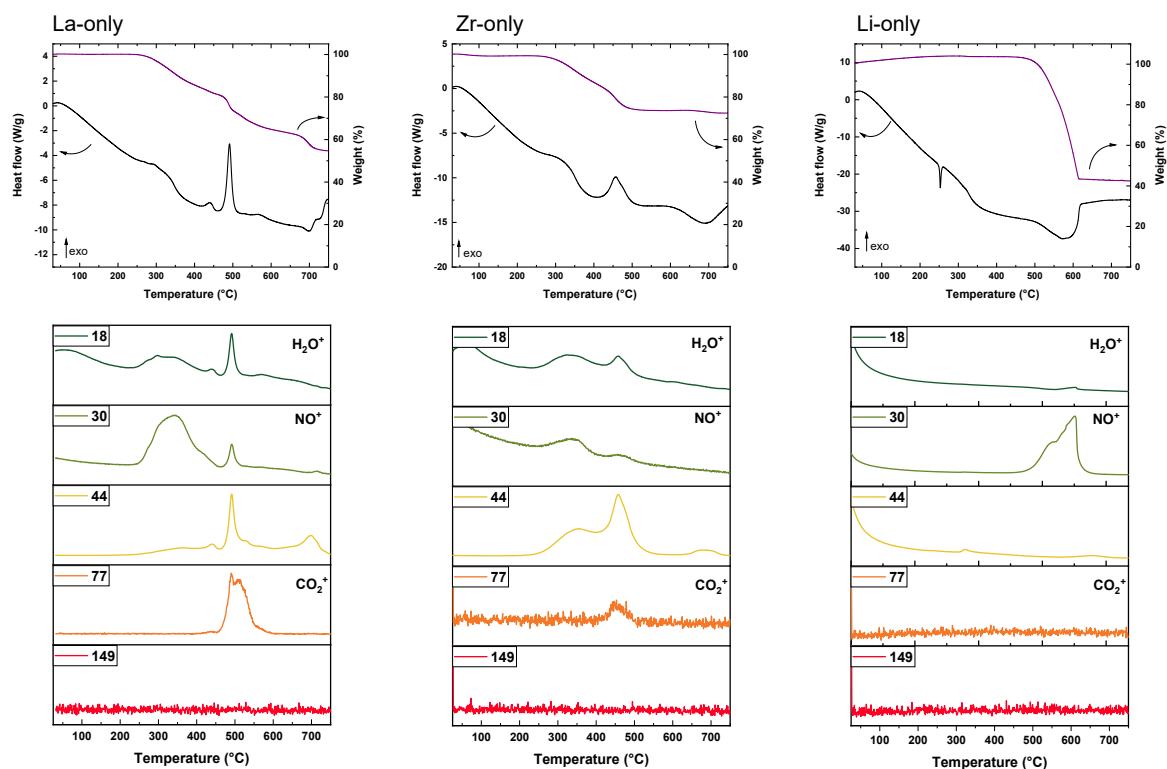


Figure S2: TGA/DSC curves of as deposited films with varying compositions and mass spectrometry of evolving gases recorded during heating to 750°C. Traces of MS fragments with a mass over charge ratio of $m/z = 18, 30, 44, 77$ and 149 are shown exemplarily for evaporation of water, decomposition of nitrates, carbonaceous compounds, aromatics and DEHP, respectively. a) La-only film, b) Zr-only film and c) Li-only film.

Table S5: Weight losses observed in STA analysis as shown in Figure S2 for the La-only film with a total weight of 5.5mg.

Step #	Temperature range (°C)	Weight loss (%)
--------	------------------------	-----------------

1	30-420	15.8
2	420-460	3.0
3	460-520	9.6
4	520-640	8.3
5	640-750	8.9
Total loss		45.6

Table S6: Weight losses observed in STA analysis as shown in Figure S2 for the Zr-only film with a total weight of 3.5mg.

Step #	Temperature range (°C)	Weight loss (%)
1	30-180	0.8
2	180-410	12.9
3	410-575	12.8
4	575-750	1.2
Total loss		27.7

Table S7: Weight losses observed in STA analysis as shown in Figure S2 for the Li-only film with a total weight of 1.4mg.

Step #	Temperature range (°C)	Weight loss (%)
1	425-650	60.5
Total loss		60.5

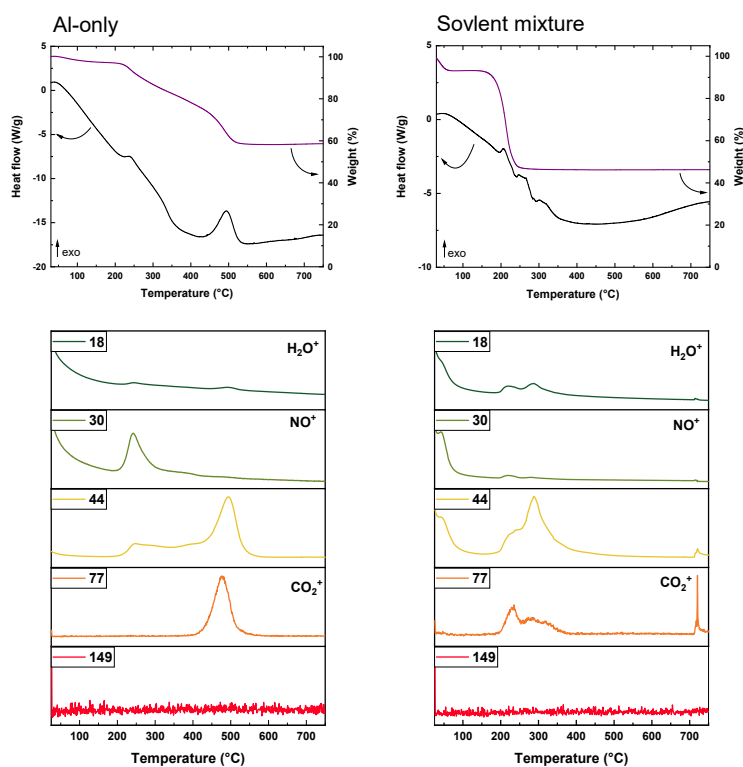


Figure S3: TGA/DSC curves of as deposited films with varying compositions and mass spectrometry of evolving gases recorded during heating to 750°C. Traces of MS fragments with a mass over charge ratio of m/z 18, 30, 44, 77 and 149 are shown exemplarily for evaporation of water, decomposition of nitrates, carbonaceous compounds, aromatics and DEHP, respectively. a) Al-only film and b) pure solvent mixture.

Table S8: Weight losses observed in STA analysis as shown in Figure S3 for the Al-only film with a total weight of 2.85mg.

Step #	Temperature range (°C)	Weight loss (%)
1	30-180	2.9
2	180-365	15.8
3	365-580	23.2
Total loss		41.9

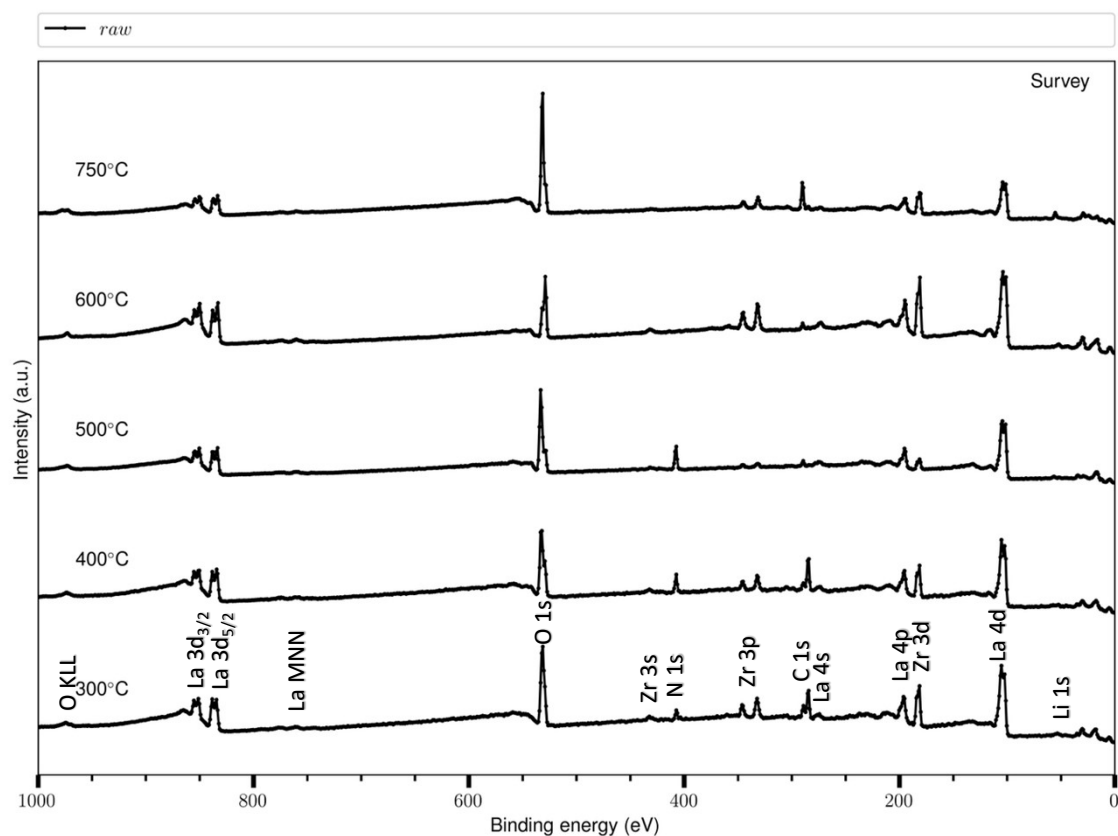


Figure S4: XPS survey spectra of LLZO films annealed at 300, 400, 500, 600 and 750 °C.

Table S9: Fitted XPS peak positions

Annealing temperature (°C)	C 1s BE (eV)	O 1s BE (eV)	N 1s BE (eV)	Li 1s BE (eV)	La 3d 5/2 BE (eV)	Zr 3d 5/2 BE (eV)
300	284.8 (C-C, C-H) 285.7 (C-OR, C-OH) 288.6 (COOR, COOH) 289.7 (CO ₃ ²⁻ adventitious)	529.5 (Oxide) 531.6 (CO ₃ ²⁻ adventitious) 532.9 (LiNO ₃)	407.3 (LiNO ₃)	56.1 (LiNO ₃)	834.4	181.8
400	284.8 (C-C, C-H) 285.7 (C-OR C-OH) 288.8 (COOR, COOH) 289.9 (CO ₃ ²⁻ adventitious)	529.3 (Oxide) 531.7 (CO ₃ ²⁻ adventitious) 533.2 (LiNO ₃)	407.5 (LiNO ₃)	56.1 (LiNO ₃)	834.0	181.5
500	289.4 (CO ₃ ²⁻ adventitious) 290.1 (Li ₂ CO ₃)	529.0 (Oxide) 531.5 (CO ₃ ²⁻ adventitious) 533.5 (LiNO ₃)	407.8 (LiNO ₃)	56.7 (LiNO ₃)	833.7	181.2
600	290.1 (Li ₂ CO ₃)	528.9 (Oxide) 529.9 (O Interstitial) 531.9 (Li ₂ CO ₃)		55.4 (Li ₂ CO ₃)	833.3	181.1
750	290.1 (Li ₂ CO ₃)	528.8 (Oxide)		55.5	833.3	180.9

		529.8 (O Interstitial) 531.9 (Li ₂ CO ₃)		(Li ₂ CO ₃)		
--	--	--	--	------------------------------------	--	--

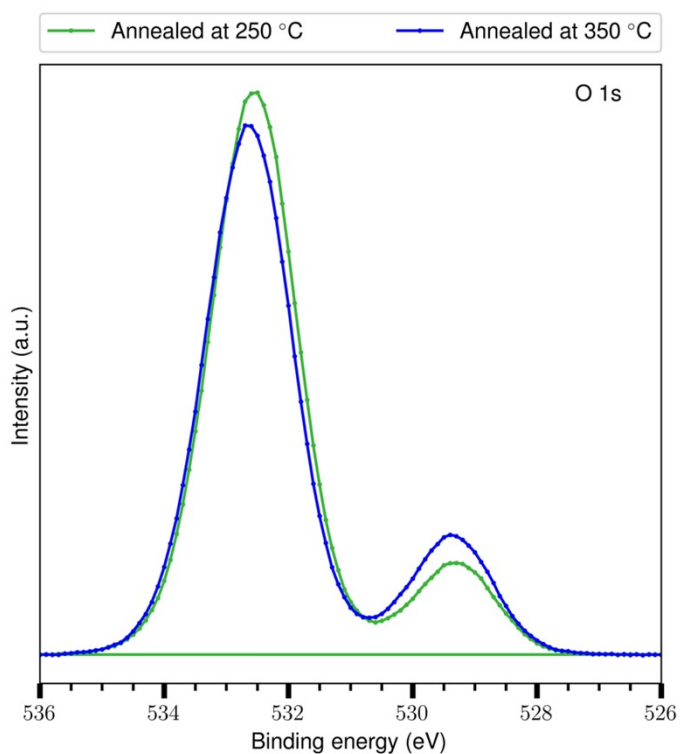


Figure S5: XPS of LLZO film annealed at 750 °C after two different post treatments inside analysis chamber. The XPS shows an increased intensity of metal oxide in O 1s region, when the film was annealed at two different temperatures to remove Li₂CO₃. Both post treatments involved first annealing in UHV, and then in 1×10^{-6} mbar O₂ at constant temperature for 30 mins each and the measurements were done at 200 °C.

Table S10: XPS quantitative analysis, relative atomic %.

Annealing temperature (°C)	O 1s (lattice)	O 1s (nitrate)	O 1s (CO ₃ ²⁻)	Zr 3d	La 4d	N 1s	C 1s	Li 1s
300	12.1	9.9	33.0	5.5	8.1	3.7	25.1	2.5
400	13.4	21.7	16.5	3.9	7.2	8.6	18.3	10.4
500	11.0	39.8	10.4	1.4	8.3	13.3	3.9	11.8
600	37.1	0.0	20.0	10.5	12.2	0.0	6.8	13.5
750	8.9	0.0	43.6	2.4	3.2	0.0	14.0	27.9

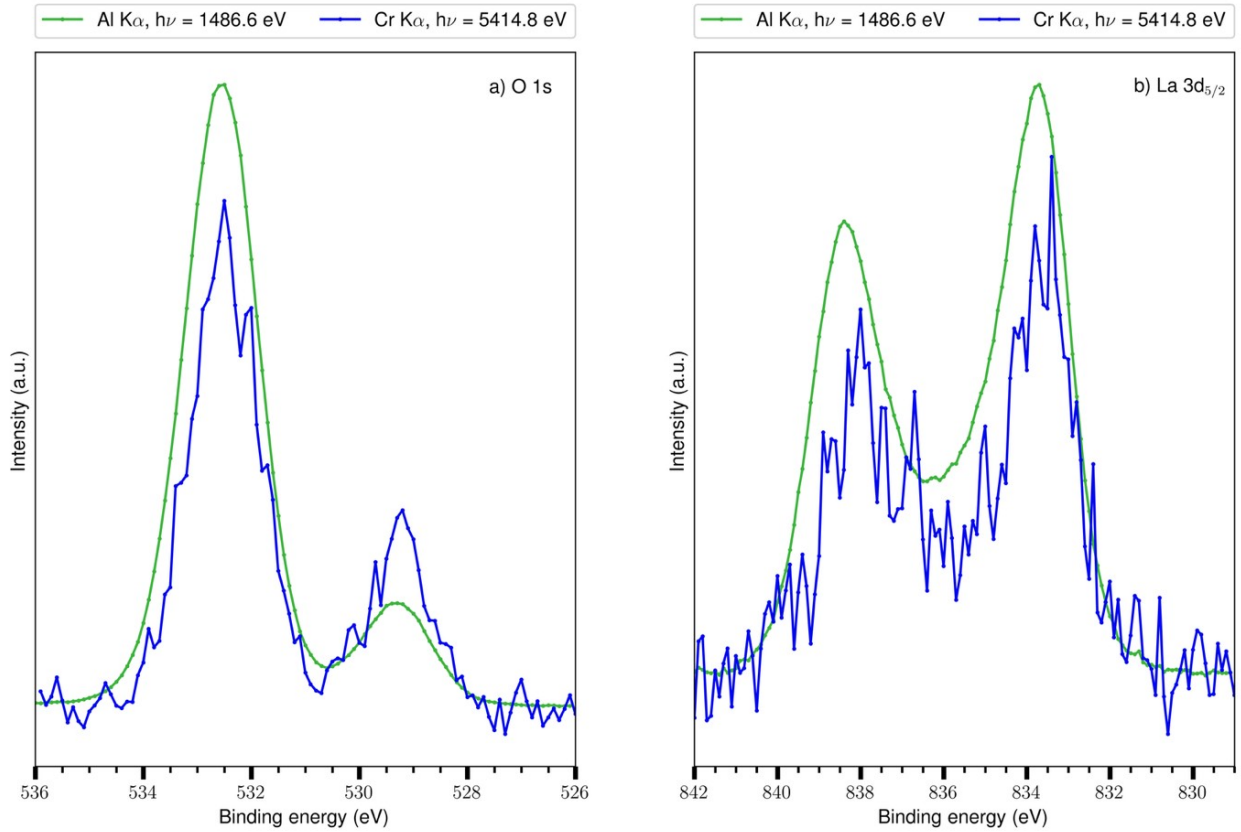


Figure S6: XPS of LLZO films annealed at 750 °C with two different X-ray excitation energy, comparing the difference between XPS (Al $K\alpha$, $h\nu = 1486.6$ eV) and HAXPES (Cr $K\alpha$, $h\nu = 5414.8$ eV) for a) O 1s and b) La $3d_{5/2}$ spectra. Comparison was performed to investigate the effect of decreasing bonding–antibonding separation in La La $3d_{5/2}$ spectra from 600 to 750°C. Measurements were performed using higher excitation X-ray energy (Cr $K\alpha$, 5414.8 eV) on this sample, enabling laboratory-based HAXPES (hard X-ray photoelectron spectroscopy). The resulting increase in probing depth—approximately threefold relative to standard XPS—facilitates investigation beneath the thin surface layers (e.g., Li_2CO_3). This is confirmed by the increased intensity of metal oxides relative to Li_2CO_3 in O 1s region. Although HAXPES enables improved detection of metal oxides covered with thin contamination layer, this comes at the expense of reduced photoionization cross-section and, consequently, lower signal intensity. Due to lower signal intensity and thus a lower signal to noise ratio, the peak fitting process becomes very difficult and worthless. A similar scenario was observed for La 3d, where the signal-to-noise ratio remained insufficient to draw definitive conclusions about the lanthanum phase or fully explain the observed reduction in bonding–antibonding separation. Thus, it remains unresolved whether the formation of LLZO directly drives these changes, necessitating further study.