Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary information

Facile Synthesis of Al-Stabilized Lithium Garnets by Solution-Combustion Technique for All Solid-State Batteries

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1. Experimental Procedure to Prepare Al-LLZO ($Li_{6.28}Al_{0.24}La_3Zr_2O_{12}$) and Fuel Solutions

For preparing Al-LLZO precursor solution, stoichiometric amounts of the (Li, La, Al) nitrate and Zr-oxynitrate in a molar ratio ~ 6.6 (5-10 % excess Li by moles) : 3: 0.24: 2 were dissolved in DI-water (amount of water required to dissolve nitrate precursor is tabulated in **Table S1**) and held under constant stirring at 80 °C until clear solution is observed. The molecular weight of ZrO (NO_3) was considered 285.23 g/mol based on hydration of the level of the precursor (~ 3 H_2O). Later, for preparing carbohydrazide (CH_6N_4O) fuel solution, amount of fuel required was determined based the combustion index of the individual precursor elements established by Jain *et al* [1]. The combustion index is a measure of the tendency of an element for combustion, which is same as its valence state. Reducing (+) and oxidizing (-) valences of the elements were used as follows to evaluate combustion index of the precursors and fuel used during the synthesis as listed below.

Reducing elements	Li, (+1), C (+4), H (+1), Al (+3), La (+3), Zr (+4)
Oxidizing elements	O (-2), N (0)

<u>The representative calculation is show below:</u>

$$\textbf{\textit{Oxidizers}}\ \{(Li_{6.5}Al_{0.24}La_3Zr_2O_{12})\} + \textbf{\textit{Fuel}}\ \{\mathbf{m}^*\ (CH_6N_4O)\} = 0 \qquad \textbf{(1)}$$

Precursors	**Combustion index**
6.6 $\{LiNO_3\}$ = 6.6 (1+ 0 + 3 x (-2))	-32.5
3 $\{La\ (NO_3)_3 \cdot 6H_2O\}$	-45
2 $\{ZrO\ (NO_3)_2 \cdot 3H_2O\}$	-20
0.24 $\{Al\ (NO_3)_3 \cdot 9H_2O\}$	-3.6
m * CH_6N_4O	8

Required **m moles** of carbohydrazide under stoichiometric condition (*i.e.* F/O =1) is calculated by balancing combustion index. From the above equation (1) we arrive at 0.079 moles of fuel. Typical amounts of fuel (at F/O value = 4) and precursors amounts required to synthesize for example 3 g of Al-LLZO powders are listed in **Table S-1.** Based on the fuel/oxidizer ratio, amount of fuel is dissolved in minimum amount of DI water held at 80 °C with constant stirring until clear solution was observed. Later, nitrate precursor solution and fuel solution are mixed and held at 80 °C under constant stirring for about 10 mins until gel is formed. Borax beaker (100 ml) containing dehydrated gel is introduced in a preheated muffle furnace **(placed inside the fume hood, away**

from flammable chemicals) held at 500 °C with furnace door was intentionally kept partially open (to prevent buildup of gases during the combustion reaction which occurs under < 3 mins). Post-combustion of the gel, as combusted powders were taken out and later crushed using an agate mortar and calcinated further using MgO crucible with closed lids between (600-900°C) for 4 h with ramp rate 5 °C/ min.

Table S1. Tabulated amounts of precursor and DI-water required to dissolve precursors and fuel to prepare for example 3 g of Al-LLZO powders at F/O- 4.

Precursors	**Amounts (g)**	**Amount of DI water (ml)**
$LiNO_3$	0.6	1.0
$La\ (NO_3)_3 \cdot 6H_2O$	1.6	1.02
$ZrO\ (NO_3)_2 \cdot 3H_2O$	0.70	10
$Al\ (NO_3)_3 \cdot 9H_2O$	0.117	0.2
CH_6N_4O	0.44	2

Table S2. Instrumental Parameters ICP-OES analysis

Thermo iCAP 6500 RAD	
RF power	1200 W
Radial observation height	12 mm
Plasma gas flow (Ar)	12 l min^{-1}
Nebulizer gas flow (Ar)	0.8 l min^{-1}
Auxiliary gas flow (Ar)	0.8 l min^{-1}
Integration time	5 s
Replicates per sample	5
Purge pump rate	1.6 ml min^{-1}
Sample flow rate	0.8 ml min^{-1}
Analytical wavelengths	
Al	396.152 nm*△
Eu (Internal standard)	281.396 nm (□) 381.967 nm (△)
La	333.749 nm□ 412.323 nm*□
Li	610.362 nm△ 670.784 nm*△
Zr	339.198 nm□ 343.823 nm*□
	* used for quantification □/△ normalized to Eu 281.396/381.967 nm signal

Table S3. Effects of fuel to oxidizer ratios on nature of combustion and phase purity of Al-LLZO on calcining at 900 °C, 4 h

F/O ratio	Combustion nature	Phases
0.5	sluggish	c-LLZO, $Li_{0.5}La_2Al_{0.5}O_4$
1	flame	c-LLZO, $Li_{0.5}La_2Al_{0.5}O_4$
2	smolder	c-LLZO, $Li_{0.5}La_2Al_{0.5}O_4$
4	smolder	c-LLZO

Table S4. Summary of phases and lattice constant of Al-LLZO calcined at various temperatures set to F/O = 4.

Calcination temperatures (°C), 4h	Phases	Lattice constant (Å)
600	c-LLZO, $La_2Li_{0.5}O_4$	13.087
700	c-LLZO, $La_2Li_{0.5}O_4$	13.046
800	c-LLZO	12.98
900	c-LLZO	12.97

Table S5. ICP-OES analysis of cubic Al-LLZO powder calcined at 800 °C / 4h and pellet sintered 1100 °C / 6 h

	Elements	**Al-LLZO powder**	**Al-LLZO Pellet**
Mass % (MV ± SD; n=3)	Al	0.59 ± 0.03	0.59 ± 0.02
	La	39.9 ± 0.7	43.4 ± 0.7
	Li	4.51 ± 0.03	4.68 ± 0.05
	Zr	18.0 ± 0.3	19.7 ± 0.3
Atomic ratio (MV ± SD; n=3)	Al/Zr	0.11 ± 0.006	0.101 ± 0.003
	Li/Zr	3.29 ± 0.005	3.12 ± 0.002
	La/Zr	1.453 ± 0.003	1.448 ± 0.004
Formula[1]		$\mathbf{Li_{6.58}\,Al_{0.22}\,La_{2.91}\,Zr_2O_{12.0}}$	$\mathbf{Li_{6.24}\,Al_{0.20}\,La_{2.89}Zr_2O_{11.8}}$

[1] Calculated, based on atomic ratios (using Zr =2 pfu as fixed point). O contents are estimated from charge balance considerations

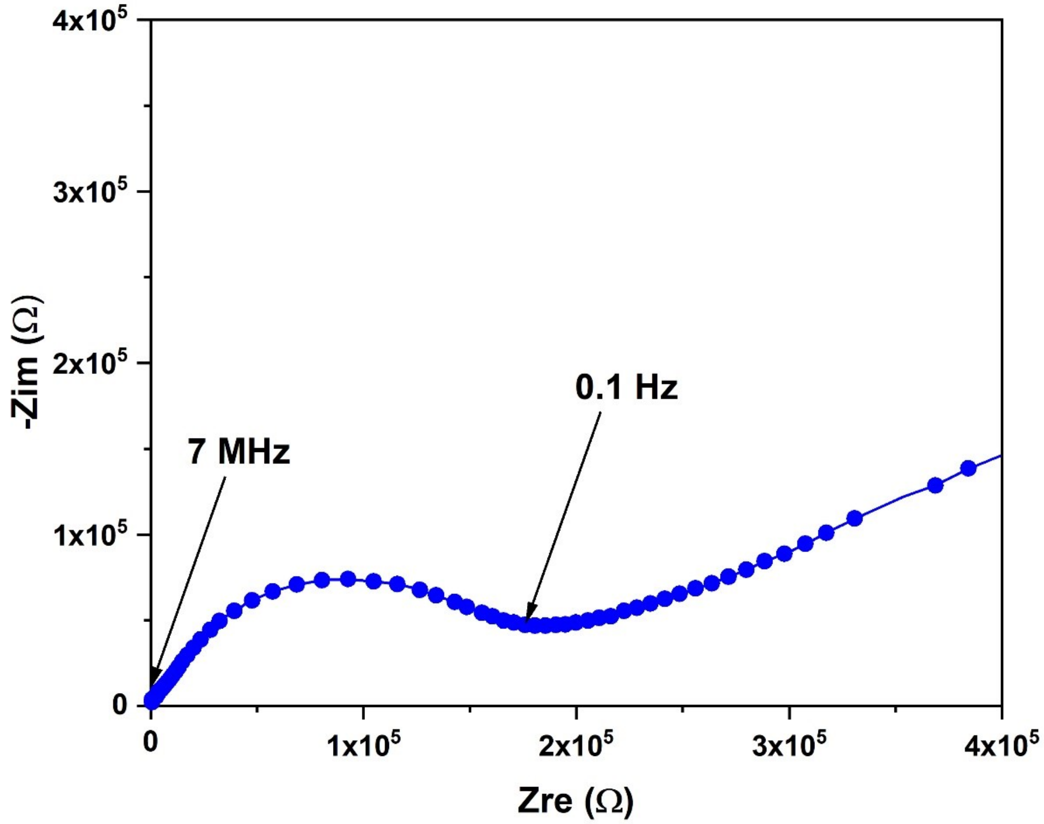

Figure S1. Nyquist plot of pellet sintered at 900 °C / 6 h representing high resistivity caused by poor densification.

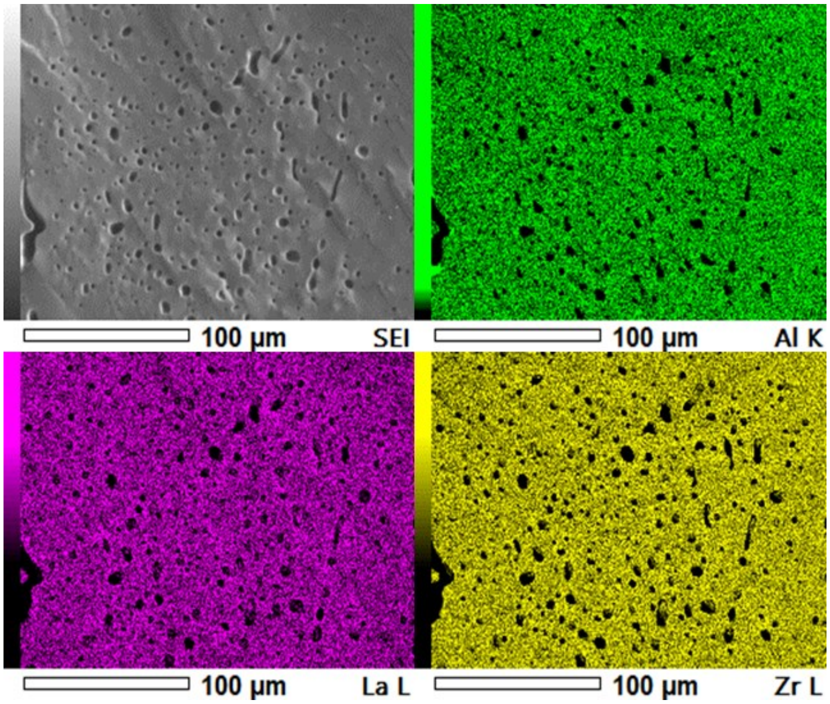

Figure S2. EDS spectral imaging of pellet sintered at 1100 ºC for 6 h showing uniform distribution of Al, La, Zr across the grain boundaries.

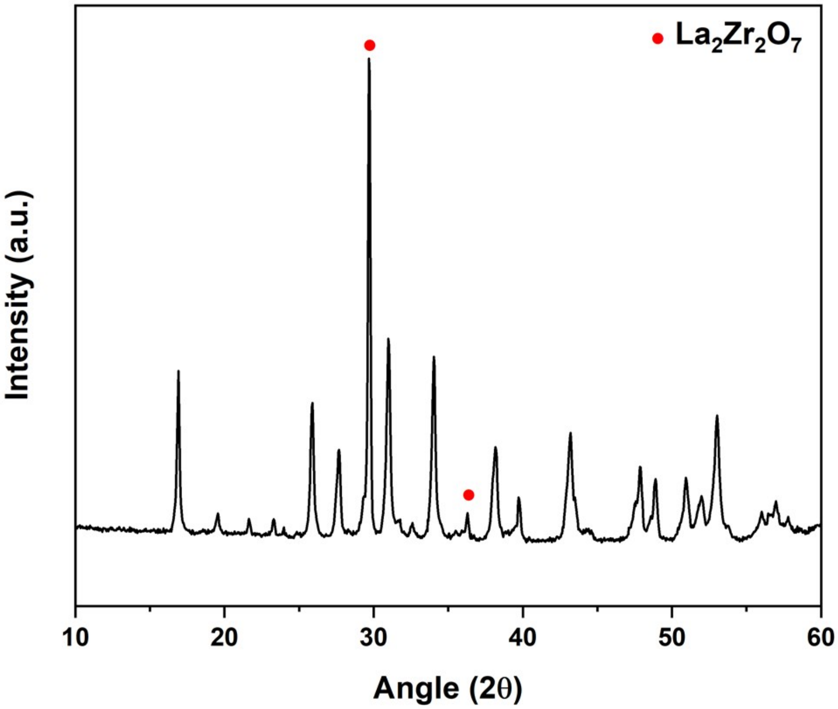

Figure S3. X-ray diffraction scan of Al-LLZO pellet sintered at 1200 °C / 6 h representing formation secondary $La_2Zr_2O_7$: (PDF card number # 00-017-0450) due to Li_2O volatilization during sintering [2].

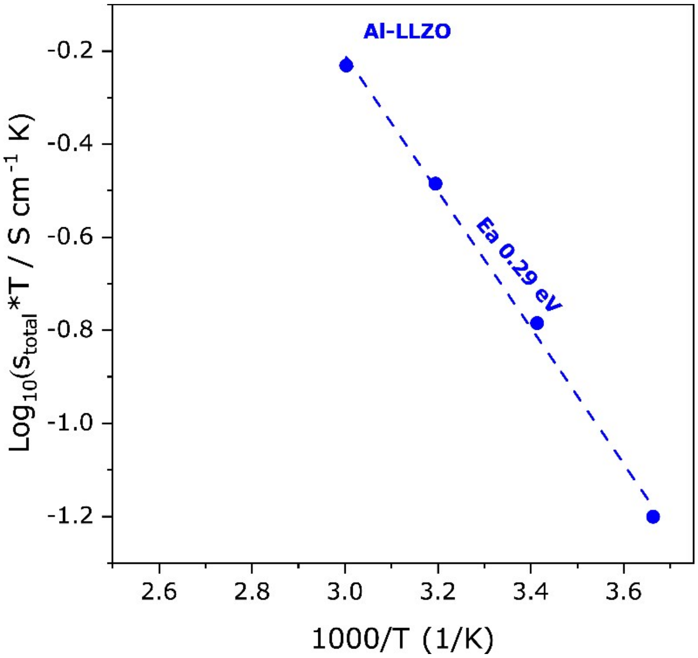

Figure S4. Temperature dependent total ionic conductivities of Al- LLZO pellet sintered at 1100 °C/ 6 h following Arrhenius trend with activation energy value 0.29 eV.

References

[ ] Jain, S. R.; Adiga, K. C.; Pai Verneker, V. R. A New Approach to Thermochemical Calculations of Condensed Fuel-Oxidizer Mixtures. *Combust. Flame.* **1981**, *40*, 71–79.

[2] Badami, P.; Weller, J. M.; Wahab, A.; Redhammer, G.; Ladenstein, L.; Rettenwander, D.; Wilkening, M.; Chan, C. K.; Kannan, A. N. M. Highly Conductive Garnet-Type Electrolytes: Access to $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ Prepared by Molten Salt and Solid-State Methods. *ACS Appl. Mater. Interfaces.* **2020**, *12*, 48580