NEXA RESEARCH INSTITUTE

Department of Materials Science & Electrochemistry

Laboratory Notebook

Daily Entry Record

Experiment ID:	NRI-2024-0047
Date:	14 November 2024
Principal Inv.:	Dr. Elena Marchetti
Team:	James Okonkwo, Priya Nair
Project:	Solid-State Electrolyte Screening

Classification: Internal Confidential | **Hazard Level:** Moderate (H272, H315) | **Version:** 1.0

This entry documents the synthesis and electrochemical characterisation of lithium-garnet composite pellets ($Li_7La_3Zr_2O_{12}$, LLZO) doped with aluminium. Conductivity measurements at ambient temperature are compared against the baseline undoped batch (NRI-2024-0041) to evaluate the effect of Al^{3+} substitution on ionic transport.

Thursday, 14 November 2024
Session 3 of 5 — Morning

NRI-2024-0047
Experiment Identifier

22.3 °C RH 44 %
Lab environment at 09:07

Researcher

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Objectives & Hypothesis

Primary Objective

Synthesise aluminium-doped LLZO pellets at two dopant concentrations (0.2 mol% and 0.4 mol% Al^{3+}) and measure their room-temperature ionic conductivities via electrochemical impedance spectroscopy (EIS) using Au-sputtered blocking electrodes.

Secondary Objectives

- Confirm cubic-phase LLZO formation via X-ray diffraction (XRD) patterns.
- Compare pellet relative densities (target $\geq 94\,\%$ of theoretical).
- Record sintering mass loss and attribute to volatile Li_2O evaporation.

Hypothesis

Al^{3+} substitution for Li^{+} at tetrahedral sites will stabilise the cubic garnet phase at room temperature, yielding an ionic conductivity $\sigma \geq 3.0 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$, consistent with the results reported by [1] and the in-house baseline of $\sigma = 1.1 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ for undoped LLZO batch NRI-2024-0041.

Related protocols: NRI-SOP-EC-07 (EIS procedure), NRI-SOP-SY-12 (solid-state synthesis), NRI-SOP-XR-03 (XRD sample prep).

Materials & Equipment

Reagents

Reagent	Grade	Supplier	Batch No.	Quantity
Li_2CO_3	99.9 %	Apex Chemicals Ltd.	APC-2024-11-07	8.42 g
La_2O_3	99.99 %	Meridian Advanced Mat.	MAM-0943	14.74 g
ZrO_2	99.5 %	Vertex Inorganics	VTX-ZR-0221	7.36 g
Al_2O_3	99.8 %	Nimbus Labs	NLB-AL-0088	0.34 g
Isopropanol (IPA)	HPLC	Synapse Reagents	SYN-IP-2024	60 mL
Ethanol (abs.)	99.8 %	Synapse Reagents	SYN-ET-2024	20 mL

Equipment

- High-energy ball mill (Nexa BM-400)
- Pellet press, 13 mm die set
- Box furnace, max. 1200 °C (NRI-F-02)
- Sputter coater (Nimbus SC-10)
- Potentiostat/galvanostat (Vertex Ivium-V)
- XRD diffractometer (Meridian X'Pert3)
- Micrometer calliper (±1 μm)
- Analytical balance (±0.01 mg)

PPE required: Safety glasses, nitrile gloves, lab coat, dust mask (P2) during powder handling. ⚠ La_2O_3 and Li-compounds are irritants — handle in fume cupboard.

Procedure

Each step is logged with start time, action, and deviations from the standard operating procedure (NRI-SOP-SY-12).

Step	Time	Stage	Action / Parameters	Deviation / Note
1	09:10	Precursor drying	La_2O_3 dried 12 h at 900 °C; cooled in desiccator. Weighed immediately after.	None.
2	09:35	Stoichiometry calc.	Nominal composition: $Li_{6.75}Al_{0.25}La_3Zr_2O_{12}$. Li excess +10 % wt to compensate sintering loss.	Al target 0.2 mol%.
3	09:50	Ball milling	Powders combined in ZrO_2 jars with 60 mL IPA. Milled at 400 rpm, 6 h, 15-min on / 5-min off cycle.	Jar changed after crack found in original jar.
4	16:05	Slurry drying	Slurry transferred to Petri dish; dried at 80 °C, 2 h in convection oven. Powder gently sieved (125 μm mesh).	None.
5	18:20	Pellet pressing	Dried powder uniaxially pressed at 250 MPa; two pellets (P-047-A, P-047-B), 13 mm diameter.	P-047-B cracked on release; discarded.
6	18:45	Calcination	P-047-A placed on MgO setter in box furnace. Ramp 5 °C min^{-1} → 1150 °C, dwell 12 h, furnace cool.	**Deviation**: furnace NRI-F-01 unavailable (maintenance); used NRI-F-02 — calibration verified.
7	Next day	Sintering complete	Retrieved after 14 h cool-down. Mass loss: 3.4 % (expected 3–5 %). Pellet intact, slight opacity.	None.

Raw Observations & Measurements

Pellet physical characterisation (after sintering, before electrodes)

Parameter	P-047-A (0.2 mol% Al)	Target	NRI-2024-0041 (baseline)
Diameter (mm)	12.84	13.00 ± 0.20	12.91
Thickness (mm)	1.37	1.2–1.6	1.41
Mass before sinter (g)	0.9143	—	0.9204
Mass after sinter (g)	0.8832	—	0.8841
Mass loss (%)	3.40	3–5	3.29
Archimedes density (g cm^{-3})	4.91	≥4.96	4.87
Relative density (%)	**92.8**	≥94	92.0
Visual appearance	Ivory, slight lustre	—	White-grey

EIS measurement conditions

Temperature: 22.3 ± 0.2 °C
Frequency range: 10^{6} to 10^{-1} Hz
AC amplitude: 10 mV (rms)
DC bias: 0 V
Electrode material: Au (sputter-coated, 50 nm)
Measurement time: 09:27 – 09:44

Impedance fit results (equivalent circuit: R_b-CPE_{gb}-CPE_{dl}):

Bulk resistance R_b: 148.3 Ω
Grain-boundary R_{gb}: 312.7 Ω
χ^2 goodness of fit: 4.2×10^{-4}
Total resistance R_{tot}: 461.0 Ω
Cell constant ℓ/A: 0.852 cm^{-1}

Derived ionic conductivity

$$\sigma = \frac{\ell}{R_{tot} \cdot A} = \frac{0.852\ \text{cm}^{-1}}{461.0\ \Omega} = 1.848 \times 10^{-3}\ \text{S cm}^{-1}$$

Uncertainty estimate: ±5 % (dominant contributor: Au electrode contact area variability). **Result exceeds hypothesis threshold.**

XRD Qualitative Observations (preliminary)

Diffractogram collected 10 ° to 70 ° 2θ at 0.02 °/step, 0.5 s/step. Major peaks consistent with cubic garnet space group $Ia\bar{3}d$. No secondary phases (tetragonal LLZO, $La_2Zr_2O_7$) detectable above noise floor. Rietveld refinement pending (Priya Nair, ETA 16 Nov).

Analysis & Interpretation

Conductivity vs. baseline

The measured total ionic conductivity of P-047-A ($\sigma = 1.85 \times 10^{-3}$ S cm^{-1}) represents a **16.8-fold improvement** over undoped batch NRI-2024-0041 ($\sigma = 1.10 \times 10^{-4}$ S cm^{-1}) and surpasses the 3.0×10^{-4} S cm^{-1} hypothesis threshold by a factor of 6.2. This result aligns with literature values for Al-doped cubic LLZO [1, 2] and confirms efficient phase stabilisation.

Grain boundary resistance

The grain-boundary contribution ($R_{gb} = 312.7\ \Omega$) accounts for 67.8 % of total impedance, indicating grain-boundary resistance as the dominant limitation. This is higher than the 55 % reported in [1]

for similar compositions, suggesting further optimisation of sintering temperature or dwell time may be beneficial. A companion experiment at 1175 °C is planned for batch NRI-2024-0050.

Relative density shortfall

Relative density of 92.8 % falls below the 94 % target. Possible causes:

- Use of furnace NRI-F-02 (deviation) — thermocouple calibrated but temperature profile across sample zone may differ from NRI-F-01.
- Insufficient milling homogeneity following jar replacement in Step 3 (milling jar changeover interrupted the programmed milling cycle by ∼18 min).

Despite the density shortfall, ionic conductivity substantially exceeds the target, suggesting that grain-boundary chemistry (Al segregation) dominates over microstructural porosity in this composition window.

Key Findings

- ✔ Cubic LLZO phase confirmed.
- ✔ $\sigma = 1.85 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$.
- ✔ Hypothesis exceeded by ×6.2.
- ✖ Relative density below target (92.8 %).
- ✖ Pellet P-047-B cracked during pressing.

Next Steps

- Rietveld refinement (P. Nair, 16 Nov).
- 0.4 mol% Al batch (NRI-2024-0048).
- SEM cross-section of P-047-A.
- Repeat with NRI-F-01 once available.
- Update project tracking in Synapse LIMS.

References

[1] Charles A. Geiger, Evgeny Alekseev, Biljana Lazic, Martin Fisch, Thomas Armbruster, Reinhard Langner, Michael Fechtelkord, Nojiri Kim, Thomas Pettke, and Werner Weppner. Crystal chemistry and stability of "li7la3zr2o12" garnet: A fast lithium-ion conductor. *Inorganic Chemistry*, 50(4):1089–1097, 2011.

[2] Ramaswamy Murugan, Venkataraman Thangadurai, and Werner Weppner. Fast lithium ion conduction in garnet-type li7la3zr2o12. *Angewandte Chemie International Edition*, 46(41):7778–7781, 2007.

Entry Sign-Off & Witnessing

I hereby certify that the experimental work, observations, and data recorded in this notebook entry (Experiment ID: **NRI-2024-0047**, date: **14 November 2024**) are accurate and a true record of work conducted in accordance with Nexa Research Institute quality and safety standards.

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Entry completed:	Witnessed:	Next entry:
14 November 2024, 20:15	15 November 2024, 09:03	NRI-2024-0048

LIMS Record: NRI-LIMS-2024-0047 | **Barcode:** NRI0047-2024-1114 | Synapse LIMS v3.4