Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information -- Evaluation of $Ga_{0.2}Li_{6.4}Nd_3Zr_2O_{12}$ garnets: exploiting dopant instability to create a mixed conductive interface to reduce interfacial resistance for all solid state batteries.

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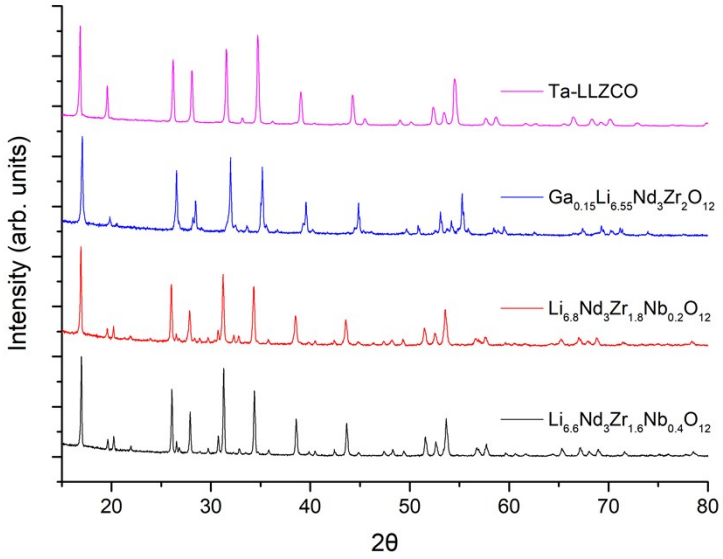
a)



b)

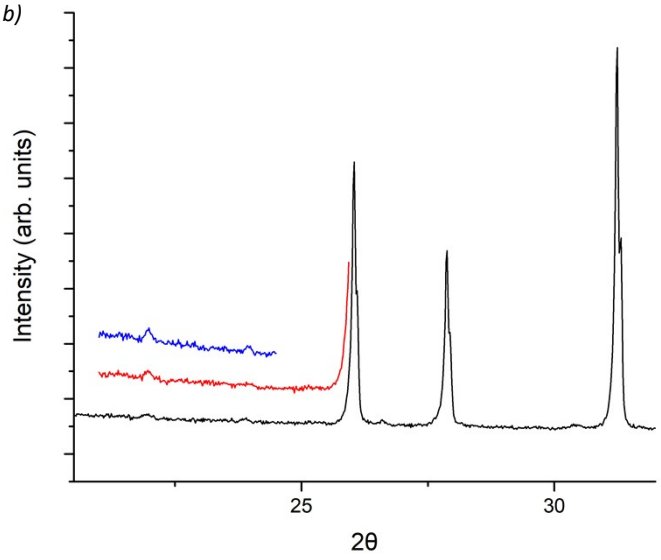


Figure S1. a) Powder XRD patterns of $Li_{6.6}Nd_3Nb_{1.6}Zr_{0.4}O_{12}$, $Li_{6.8}Nd_3Nb_{1.8}Zr_{0.2}O_{12}$ and $Li_{6.55}Ga_{0.15}Nd_3Zr_2O_{12}$. All underwent additional heating cycles and were still impure. $Li_{6.6}Nd_3Nb_{1.6}Zr_{0.4}O_{12}$ and $Li_{6.8}Nd_3Nb_{1.8}Zr_{0.2}O_{12}$ demonstrate Zr and Nb based impurities, whereas $Li_{6.4}Ga_{0.15}Nd_3Zr_2O_{12}$ has a considerable tetragonal component. The PXRD of Ta-LLZCO is also shown. b) narrow 2ϑ scans showing a small peak at ~22 2ϑ in Ga-NLZO, hence suggesting the system has I-43d type symmetry, further work is needed to confirm this.

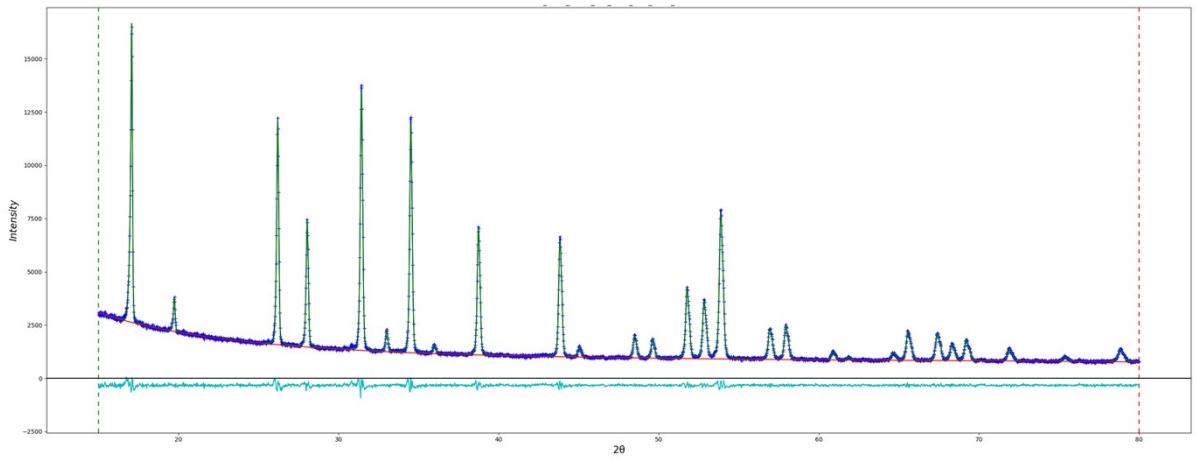


Figure S2. Example refinement of a Nd based lithium garnet; the above example is $Li_{6.2}Nd_3Zr_{1.2}Nb_{0.8}O_{12}$.

Sample (50°C)	C_{Bulk} (F cm^{-1})	ε_r
$Li_5Nd_3Nb_2O_{12}$	9.3 x10^{-12}	105
$Li_{5.5}Nd_3Zr_{0.5}Nb_{1.5}O_{12}$	4.2 x10^{-12}	47
$Li_{5.75}Nd_3Zr_{0.75}Nb_{1.25}O_{12}$	5.9 x10^{-12}	67
$Li_{6.2}Nd_3Zr_{1.2}Nb_{0.8}O_{12}$	7.9 x10^{-12}	89
$Li_{6.4}Nd_3Zr_{1.4}Nb_{0.6}O_{12}$	4.55 x10^{-12}	51
Al-NLZO	2.1 x10^{-11}	239
Ga-NLZO (18°C)	4.6 x10^{-12}	52

Table S1. Bulk capacitances and dielectric constants derived from the impedance spectra of the Nd based lithium garnets.

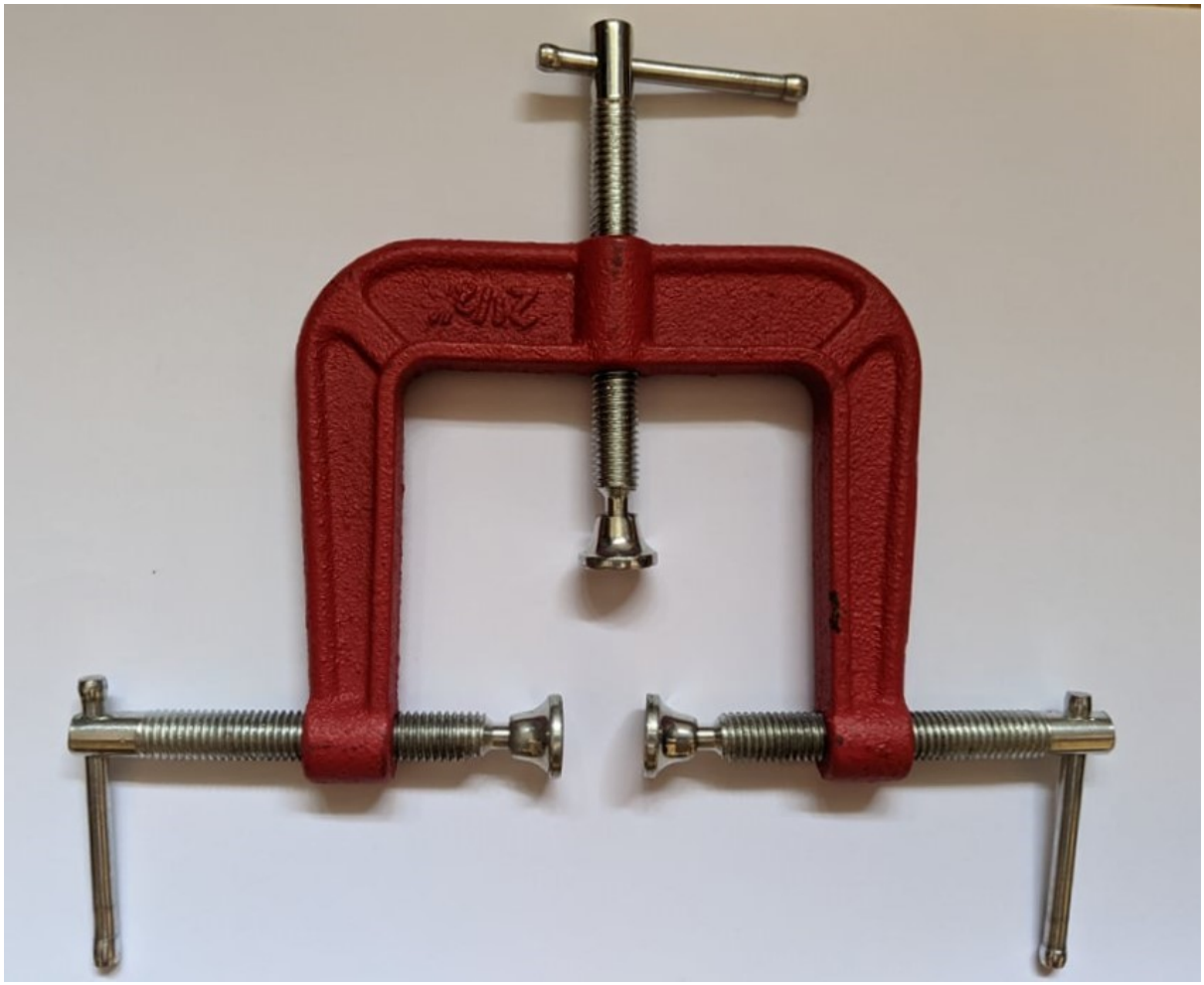


Figure S3. 2½ inch 3-way G-clamp used to form Li symmetry cells (Cu foil was used to cover the contact area to prevent cell adhering to the clamp).

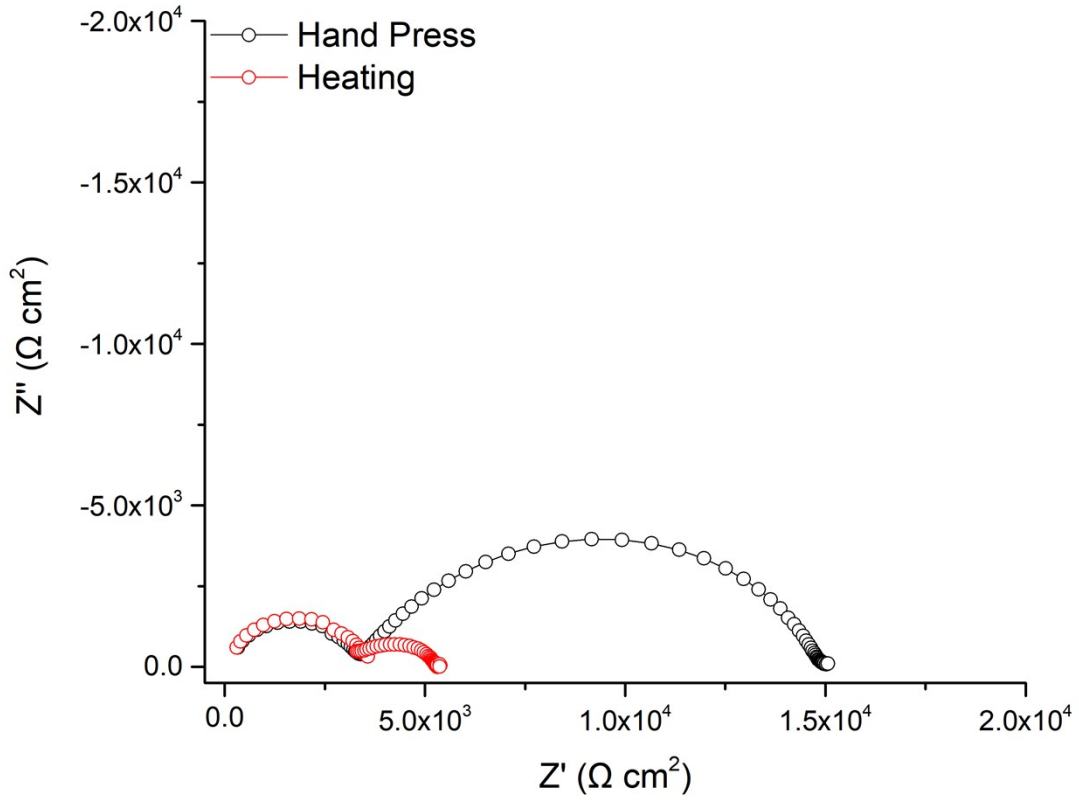


Figure S4. Tetragonal NLZO symmetry cell, pressed via hand and by heating as per the methods section. Both cases illustrate substantially higher Li/Garnet interfacial resistance when compared to Ga-NLZO at 5830 (hand pressed) and 949 (heated) Ω cm^2. This further confirms the low resistance encountered with Ga-NLZO is due to the presence of Ga in the system.

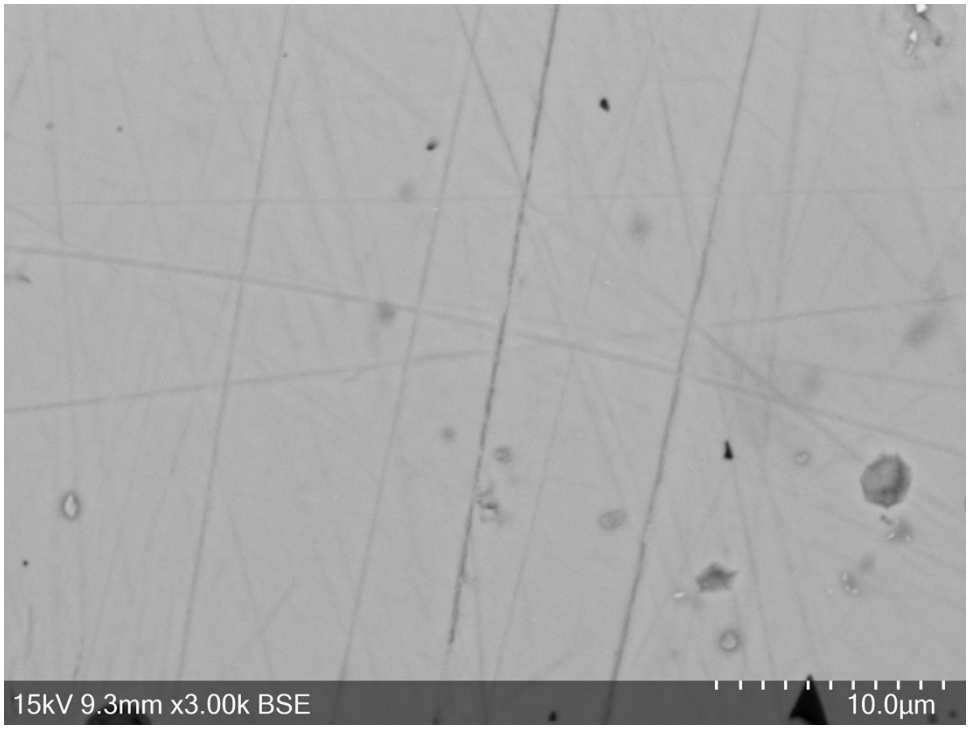


Figure S5. SEM image of post cycled Li/Ga-NLZO/Li before thermal etching, illustrating no discernible features and large scratches due to polishing of the pellets prior to assembling the symmetry cell.

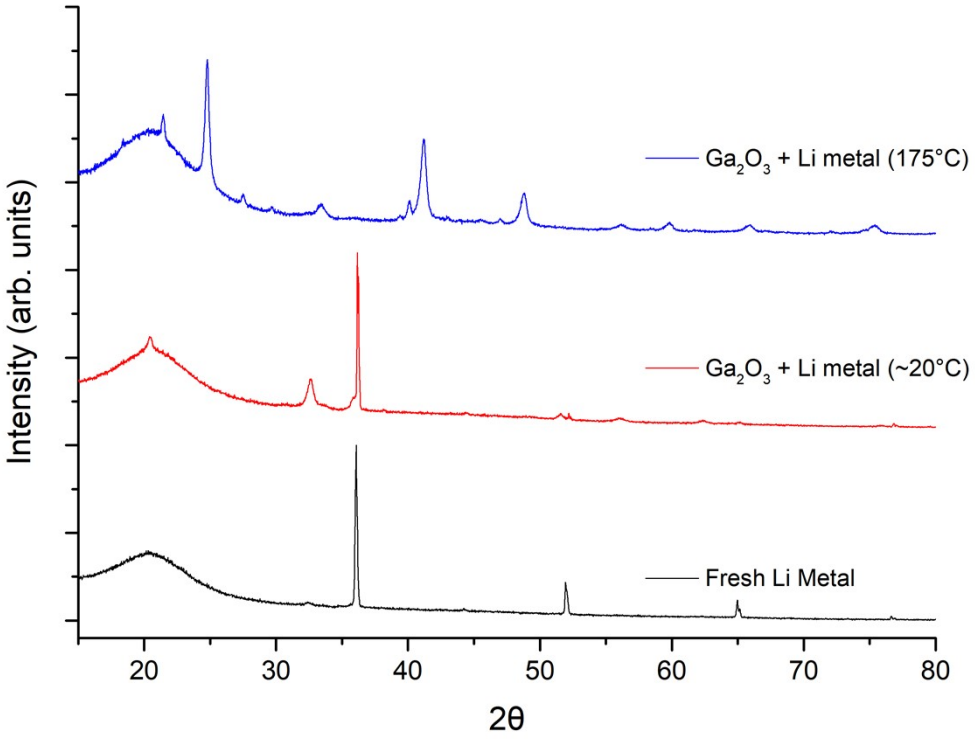


Figure S6. Reaction of Ga_2O_3 with Li metal when heated to 175°C (1h) (blue) and when left in contact with Ga_2O_3 pellet for two days (red). Pellets were uniaxially pressed to ~3 tonnes and placed in contact without any additional pressure. Black line is fresh Li metal for comparison. Ga_2O_3 + Li metal heated to 175°C illustrated evidence of Li_2Ga (stars) and GaLi (triangle) eutectic mixtures, in addition to a small amount of Ga_2O_3 powder residue from the pellet (unmarked).