Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information for:

Impact of thermal treatment on the Li-ion transport, interfacial properties, and composite preparation of Nb-doped LLZO garnets for solid-state electrolytes

Pedram Ghorbanzade [a,b], Arianna Pesce [a], Kerman Gomez [a], Grazia Accardo [a], Shanmukaraj Devaraj [a], Pedro López-Aranguren [a] and Juan Miguel López del Amo [a*]

[a.] *Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park,Albert Einstein 48, 01510 Vitoria-Gasteiz, Spain.*

[b.] *University of Basque Country (UPV/EHU), Barrio Sarriena, s/n, 48940 Leioa, Spain*

**Email: jmlopez@cicenergigune.com*

Saturation recovery experiment

Table S. 1 Fitting parameters of saturation recovery experiment presented in Figure 5.c

Sample	First component		Second component	
	Fraction (%)	T_1 (s)	Fraction (%)	T_1 (s)
T-Pristine	70 ± 1.0	16.9 ± 0.3	30 ± 1.4	103 ± 3.3
T-350	52 ± 0.5	3.9 ± 0.1	48 ± 0.5	103 ± 3.2
T-550	97 ± 0.4	0.60 ± 0.0	3 ± 0.3	22 ± 7
T-750	100	0.58 ± 0.0	---	

Although the fitting with a double exponential decay function involves some error, however two different relaxation times, one very short and the other very long are obtained for T-Pristine, T-350, and T-550. For the case of T-750, only a single exponential term is enough for the fitting as all the Li_2CO_3 (with long T_1) are eliminated.

ICP measurement

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) was applied to measure the concentration of Li in each of the samples. The powders were dissolved in 2wt% HNO_3 aqueous solution to obtain Li concentration of 50 ppm.

Table S. 2 Li+ concentration for T-Pristine, T-350, T-550, T-750 in the same mass.

Sample	$[Li^+]$ (ppm)*
T-Pristine	44
T-350	47
T-550	47
T-750	54

***** The theoretical $[Li^+]$ calculated for T-Pristine was 50 ppm.

The elimination of LiOH, water, and Li_2CO_3 from the garnet surface, as well as the protons in the bulk of garnet during the heat treatment, explain the alterations of $[Li^+]$ presented in Table SI.1. From the results, we can conclude that no Li loss (through Li_2O evaporation) is involved during the heat treatment.

^{1}H-^{1}H EXSY NMR experiment

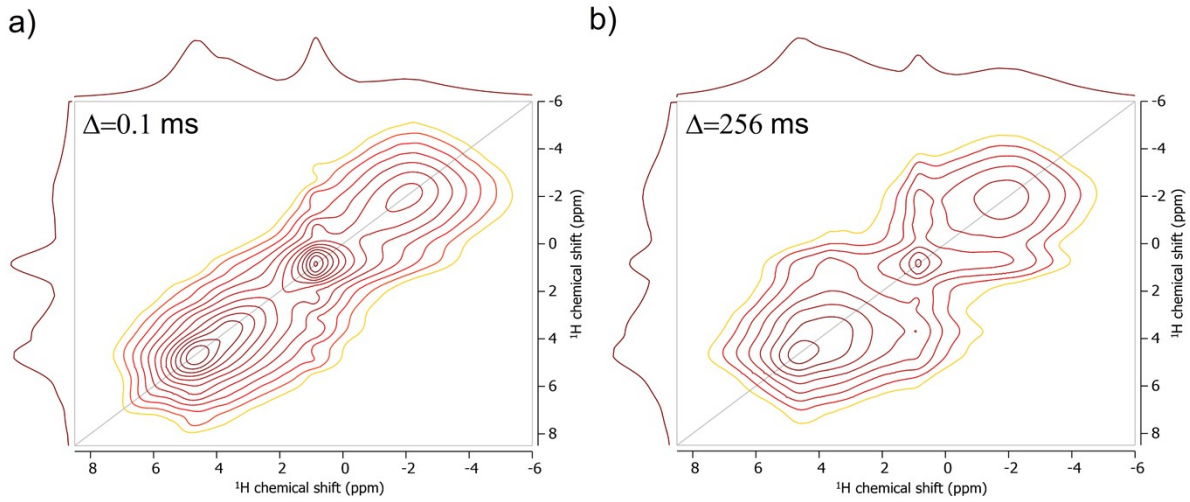

Figure S. 1 ^{1}H-^{1}H EXSY NMR experiment with a) mixing time = 0.1 ms and b) mixing time = 256 ms

Bulk ionic conductivity of sintered pellets

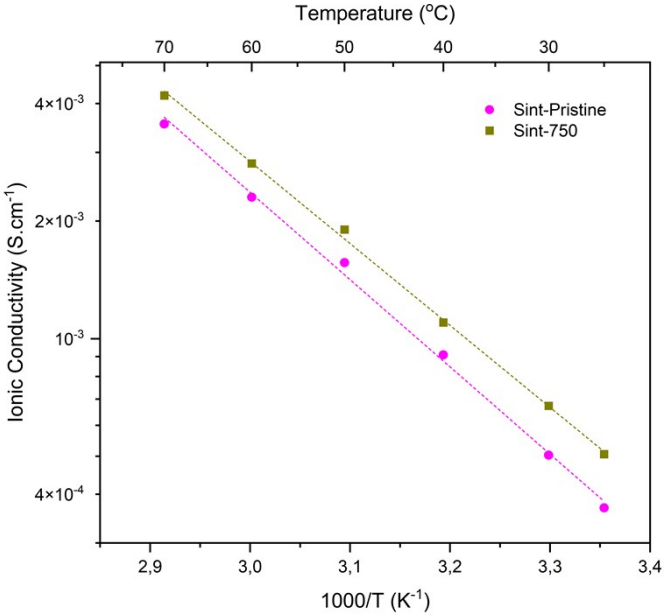

Figure S. 2 Arrhenius plot of bulk ionic conductivities of Sint-Pristine and Sint-750

Electrochemical Impedance Spectroscopy (EIS) of Composites with 90wt% LLZO content

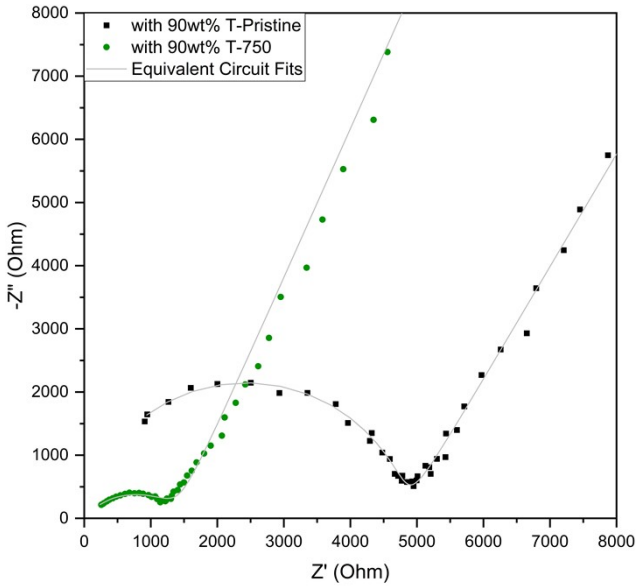

Figure S. 3 Impedance spectra of garnet-rich composite electrolytes with 90wt% T-Pristine and T-750 at 70°C

Impact of heat treatment on Al-LLZO

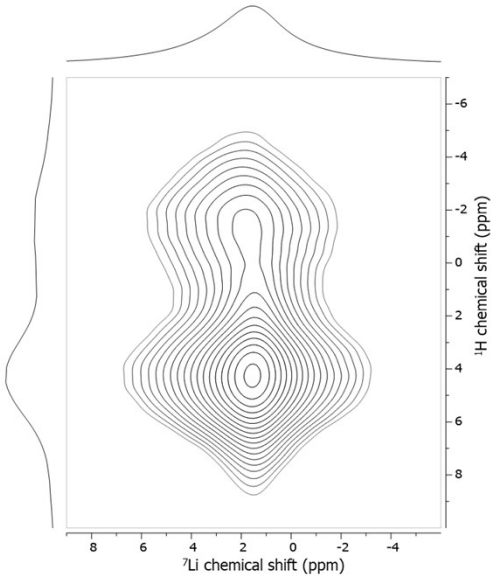

Figure S. 4 ^{7}Li-^{1}H Heteronuclear correlation of Al-LLZO before heat treatment

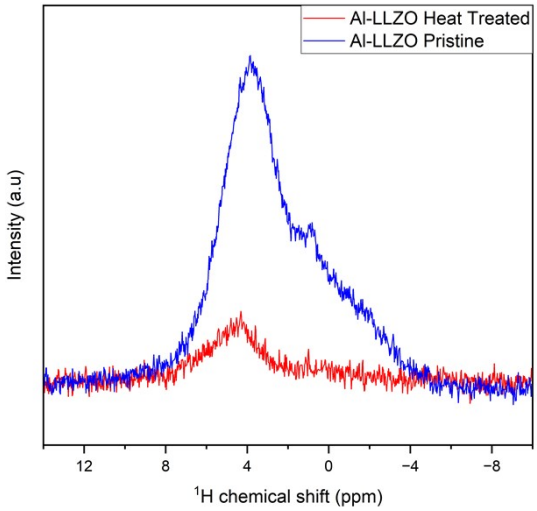

Figure S. 5 ^{1}H NMR spectra of Al-LLZO, before and after heat treatment at 750°C

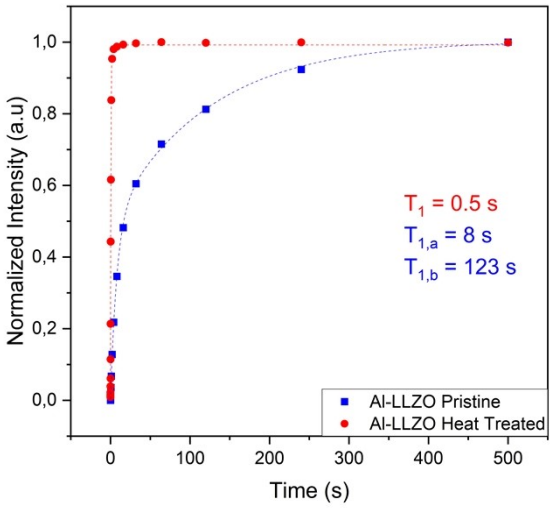

Figure S. 6 Saturation recovery and T_1 relaxation time of Al-LLZO before and after heat treatment at 750°C

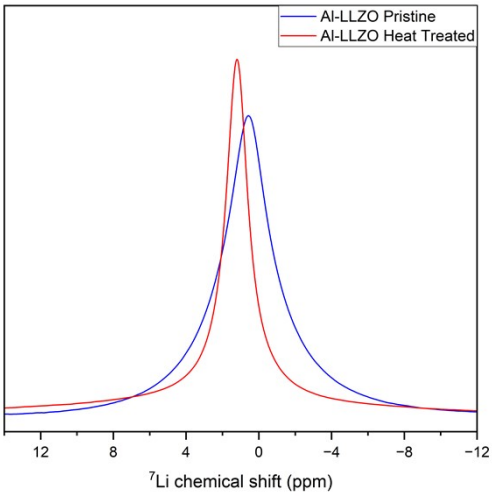

Figure S. 7 ^{7}Li NMR spectra of Al-LLZO before and after heat treatment at 750°C