Electronic Supporting Information

Fast microwave-assisted synthesis of Li-stuffed garnets and investigation of Li diffusion by muon spin spectroscopy

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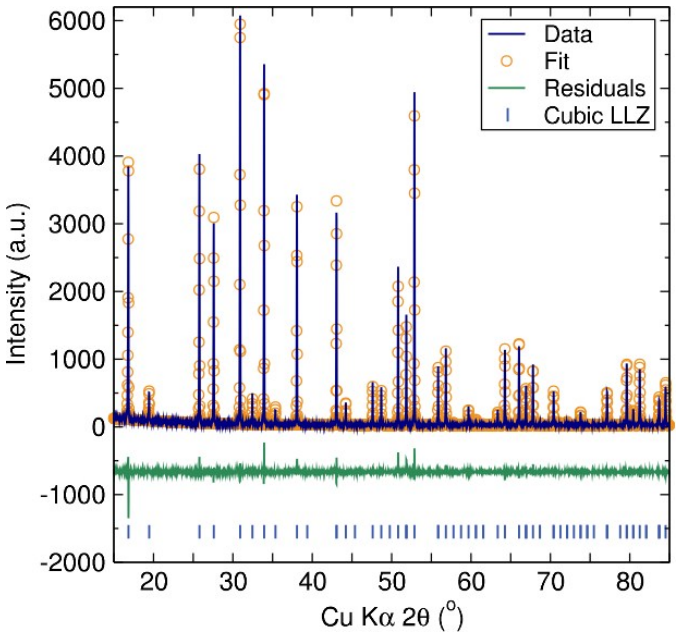


Atom	Site	Frac.	x	y	z	Uiso (100/Å)
Li1	24d	0.540	-0.125000	0.000000	0.250000	0.95(5)
Li2	96h	0.370	0.100400	0.685300	0.576900	0.93(5)
Al	24d	0.08	-0.125000	0.000000	0.250000	0.95(5)
La	24c	0.988(8)	0.000000	0.250000	0.125000	0. 90(5)
Zr	16a	1.01(1)	0.000000	0.000000	0.000000	0.90(5)
O	96h	1.000	-0.0371(4)	0.0526(4)	0.1518(4)	0.91(5)

Figure S1: Rietveld refinement and extracted parameters for PXRD data for the $Li_{6.5}Al_{0.25}La_{2.92}Zr_2O_{12}$ fit to the cubic ($Ia\bar{3}d$) space group.[1] R_{wp} = 0.1346, R_p = 0.0976, X^2 = 1.674 and R_F^2 = 0.0515.

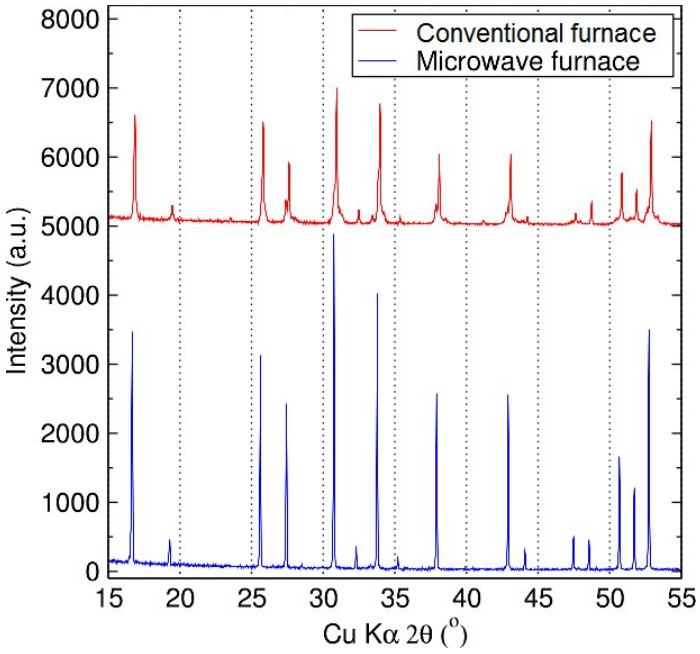


Figure S2: PXRD pattern of the as-synthesized $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ garnet by microwave-assisted vs conventional solid-state approach. Both samples where heated during 6 hours at 700 °C and a further 6 hours at 950 °C.

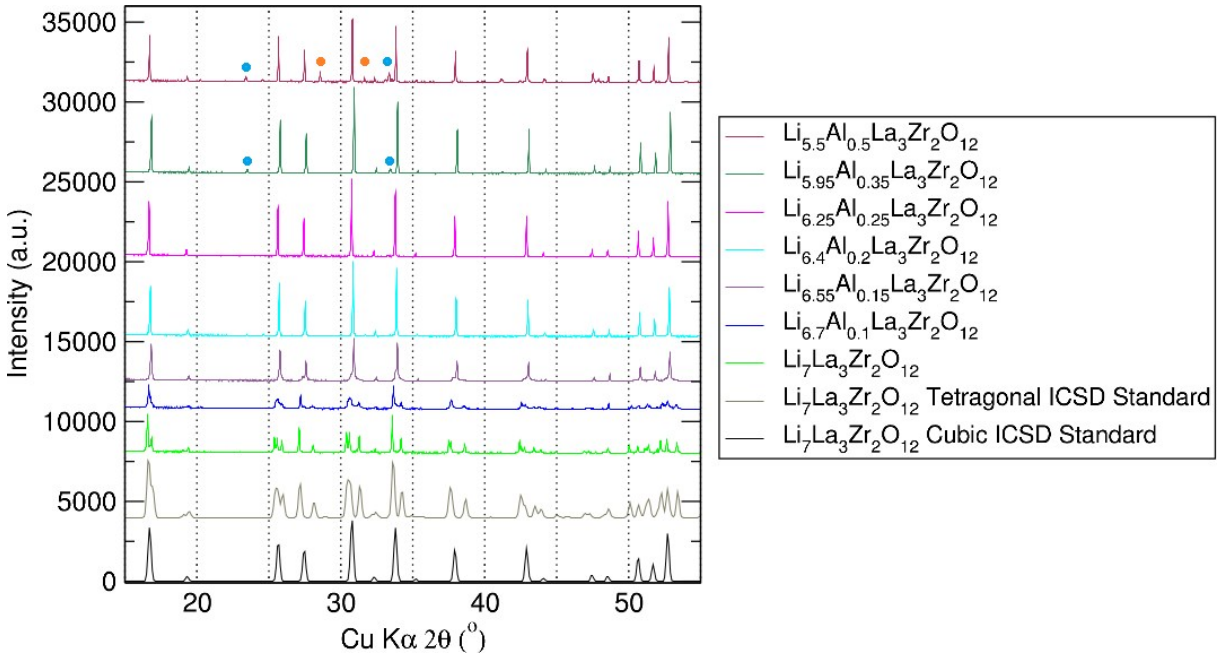
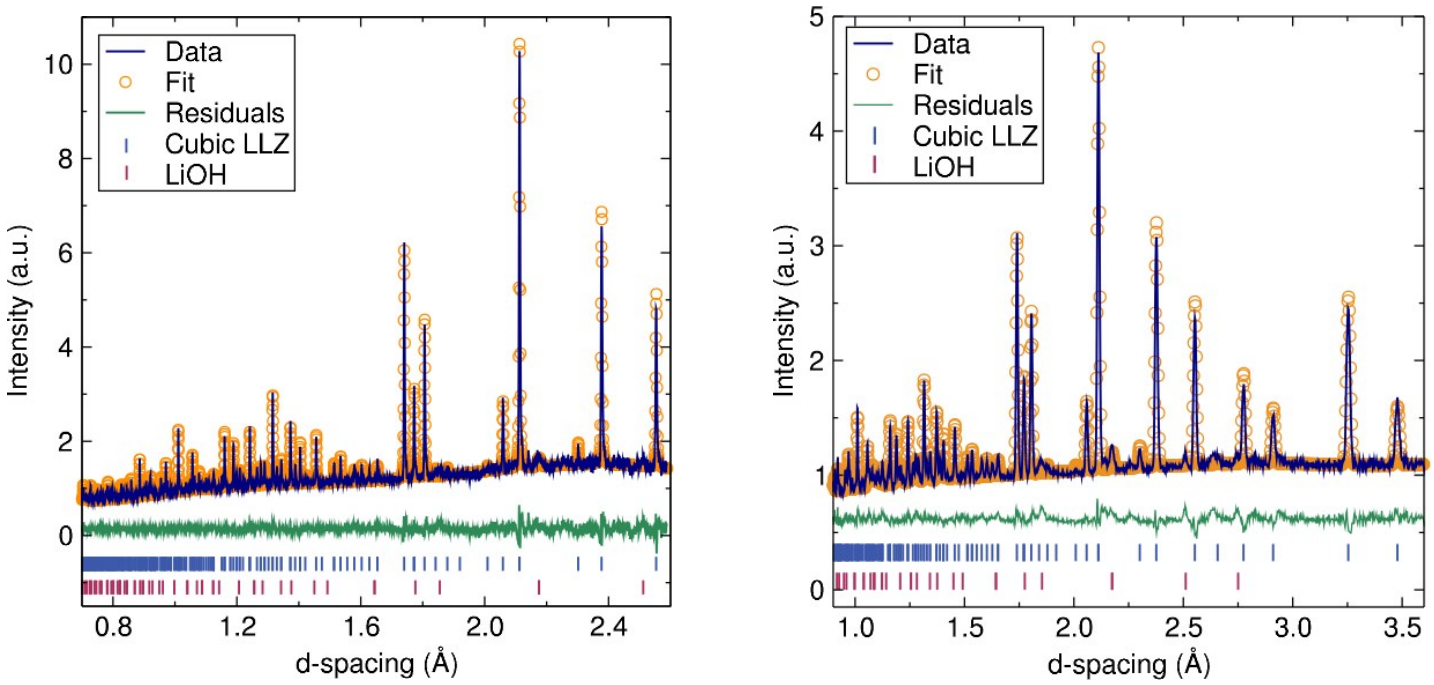


Figure S3: PXRD patterns for the LLZ garnet with increasing Al concentration from bottom to top. Reference patterns are included for the cubic ($Ia\bar{3}d$) and tetragonal ($I4_1/acd$) symmetries.[1,2] Blue dots denote $LaAlO_3$ impurity and orange dots denote $La_2Zr_2O_7$ impurity.



Atom	Site	Frac.	x	y	z	Uiso (100/Å)
Li1	24d	0.30(3)	-0.125000	0.000000	0.250000	2.3(1)
Li2	96h	0.45(1)	0.100100	0.671100	0634100	2.3(1)
Al	24d	0.077	-0.125000	0.000000	0.250000	3.2(1)
La	24c	0.973	0.000000	0.250000	0.125000	0.35(4)
Zr	16a	1.01(1)	0.000000	0.000000	0.000000	1.14(5)
O	96h	1.000	-0.03186(9)	0.0561(1)	0.1481(1)	0.80(3)

Figure S4: Rietveld refinements and extracted parameters for NPD data for the $Li_{6.5}Al_{0.25}La_{2.92}Zr_2O_{12}$ fit to the cubic ($Ia\bar{3}d$) space group and LiOH with P4/nmm symmetry.[1,3] Backscattering detector (top left): R_{wp} = 0.0377, R_p = 0.0377 and R_F^2 = 0.1120. Orthogonal detector (top right) R_{wp} = 0.0254, R_p = 0.0222 and R_F^2 = 0.1604. Reduced X^2 = 3.119. Different refined parameters (bottom table) where Al fraction was fixed to the value obtained by ICP-MS

Temp. (K)	I-G Ionic Cond. (S cm^{-1})	GB Ionic Cond. (S cm^{-1})	Total Cond. (S cm^{-1})
298	3.74×10^{-6}	4.41×10^{-9}	4.40×10^{-9}
338	4.33×10^{-6}	3.21×10^{-8}	3.19×10^{-8}
378	-	-	2.53×10^{-7}
418	-	-	9.09×10^{-7}
458	-	-	6.23×10^{-6}

Table S1: Ionic conductivity values obtained from EIS at different temperatures for the Intra-Grain (I-G) and Grain Boundary (GB) components and total ionic conductivity.

	Hopping Pathway	N_i	$Z_{v,1}$	s_i (m)	D_{Li}/v (cm^2)
D_{Li1}	24d to 96h	4	0.70	1.67×10^{-10}	4.88×10^{-21}
D_{Li2}	96h to 24d	2	0.55	1.67×10^{-10}	7.67×10^{-21}
$\sum D_{Li1,2,}/v = 1.26 \times 10^{-20}$ cm^2					

Table S1: Structural parameters employed for the calculation of the diffusion coefficient for Li ions, obtained from Rietveld refinements of PXRD and NPD.

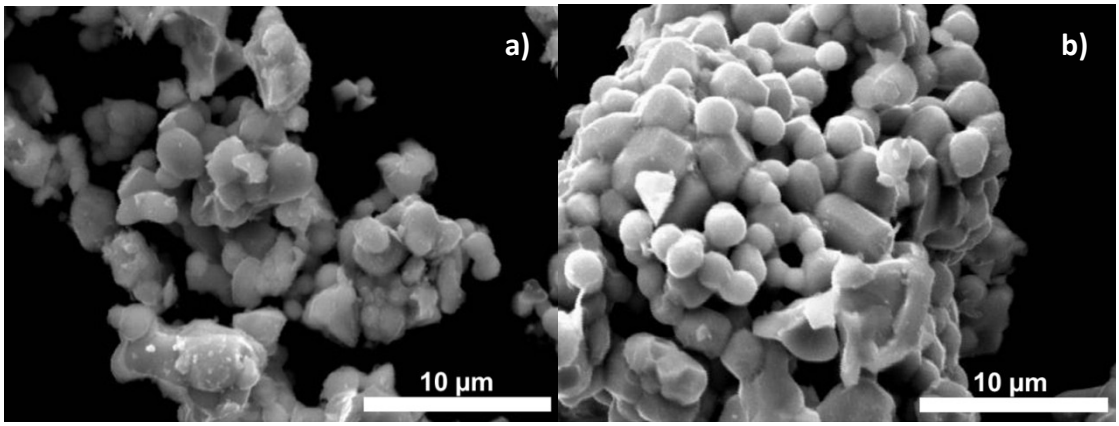


Figure S5: SEM images of the Al-doped LLZ sample prepared via microwave-assisted (a) and conventional (b) solid-state approaches. The mean particle size for the microwave-assisted prepared samples is 1.5 ± 0.4 µm while for the sample prepared via conventional solid-state approach displays an average particle size slightly bigger of 2.3 ± 0.9 µm.

References

1. R. Murugan, V. Thangadurai, W. Weppner, *Angew. Chem., Int. Ed*. **2007**, 46, 7778
2. A. Logéat, T. Köhler, U. Eisele, B. Stiaszny, A. Harzer, M. Tovar, A. Senyshyn, H. Ehrenberg, B. Kozinsky*, Solid State Ionics* **2012**, 206, 33
3. S. L. Mair, *Acta Crystallogr., Sect. A* **1978**, 34, 542