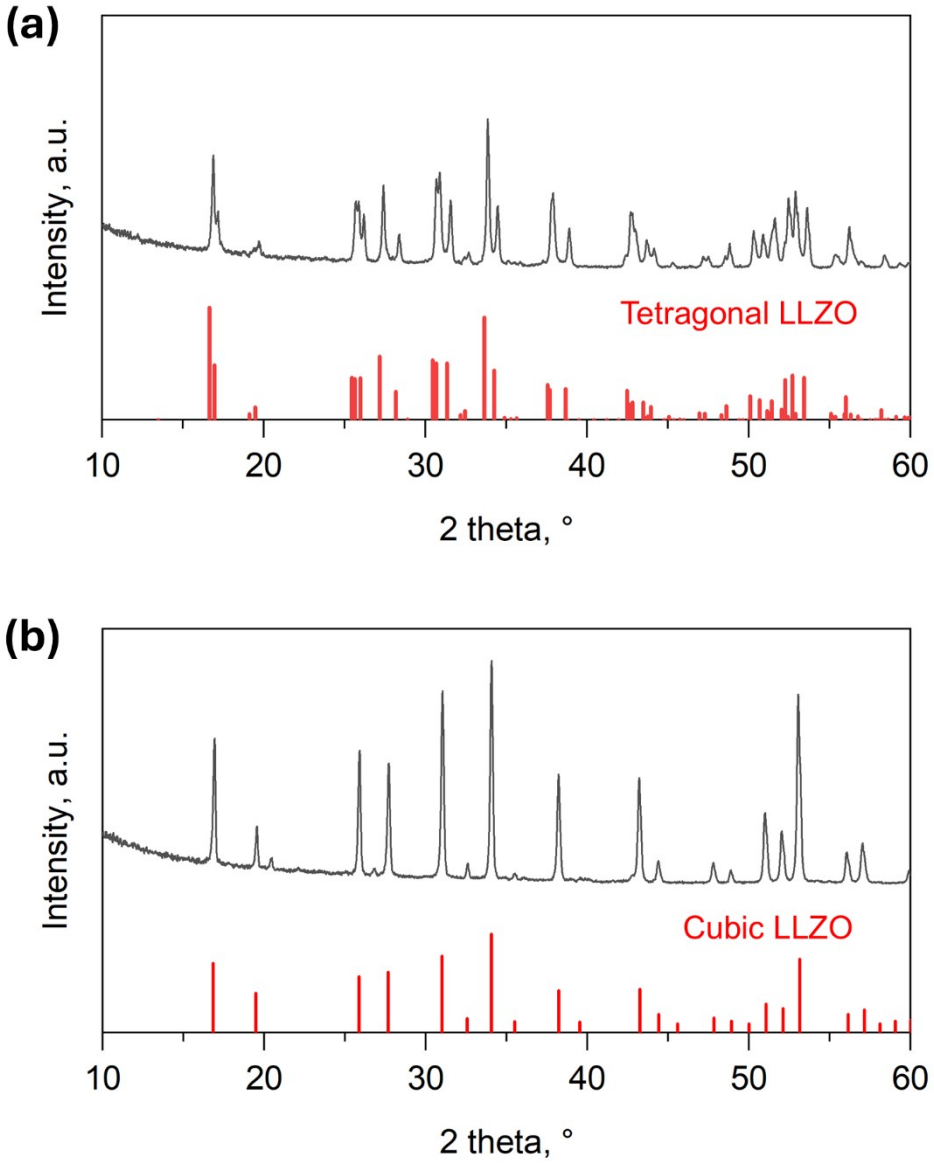

Figure S1. XRD patterns of (a) $Li_7La_3Zr_2O_{12}$ (b) $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$

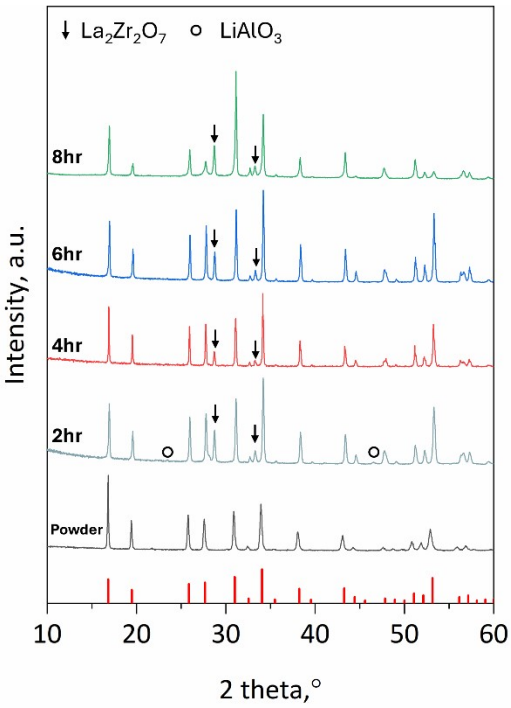

Figure S2. XRD patterns of Al0.1 doped LLZNTH ($Li_{5.7}Al_{0.1}La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$) samples, including the as-prepared powder and pellets sintered at 1200ºC for 2, 4, 6, and 8 hours.

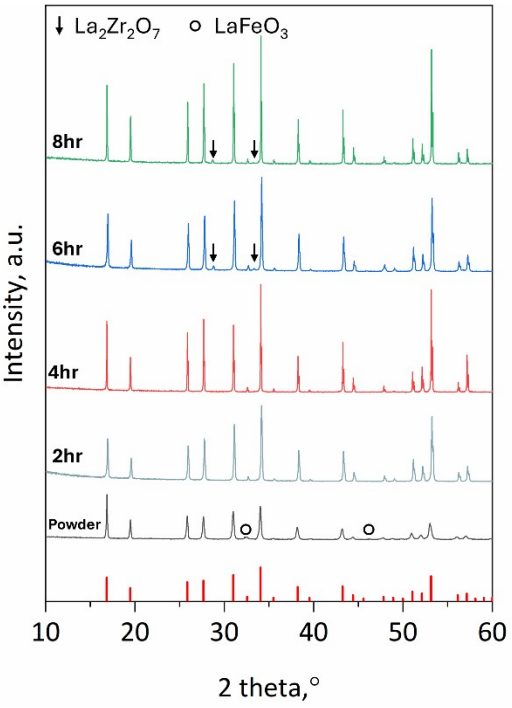

Figure S3. XRD patterns of Fe0.1 doped LLZNTH ($Li_{5.7}Fe_{0.1}La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$) samples, including the as-prepared powder and pellets sintered at 1200ºC for 2, 4, 6, and 8 hours.

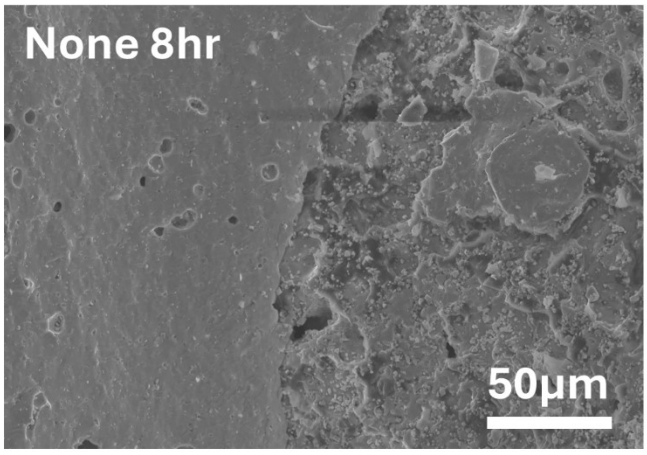

Figure S4. A SEM micrograph for the non-doped LLZNTH sintered at 1200ºC for 8 hours

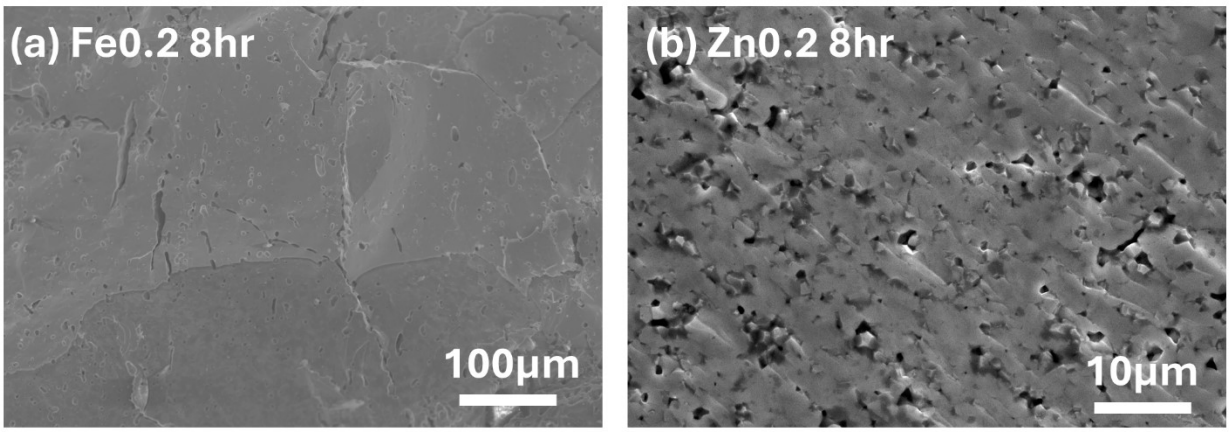

Figure S5. SEM micrographs for the Fe0.2 and Zn0.2 sintered at 1200 ºC for 8 hours

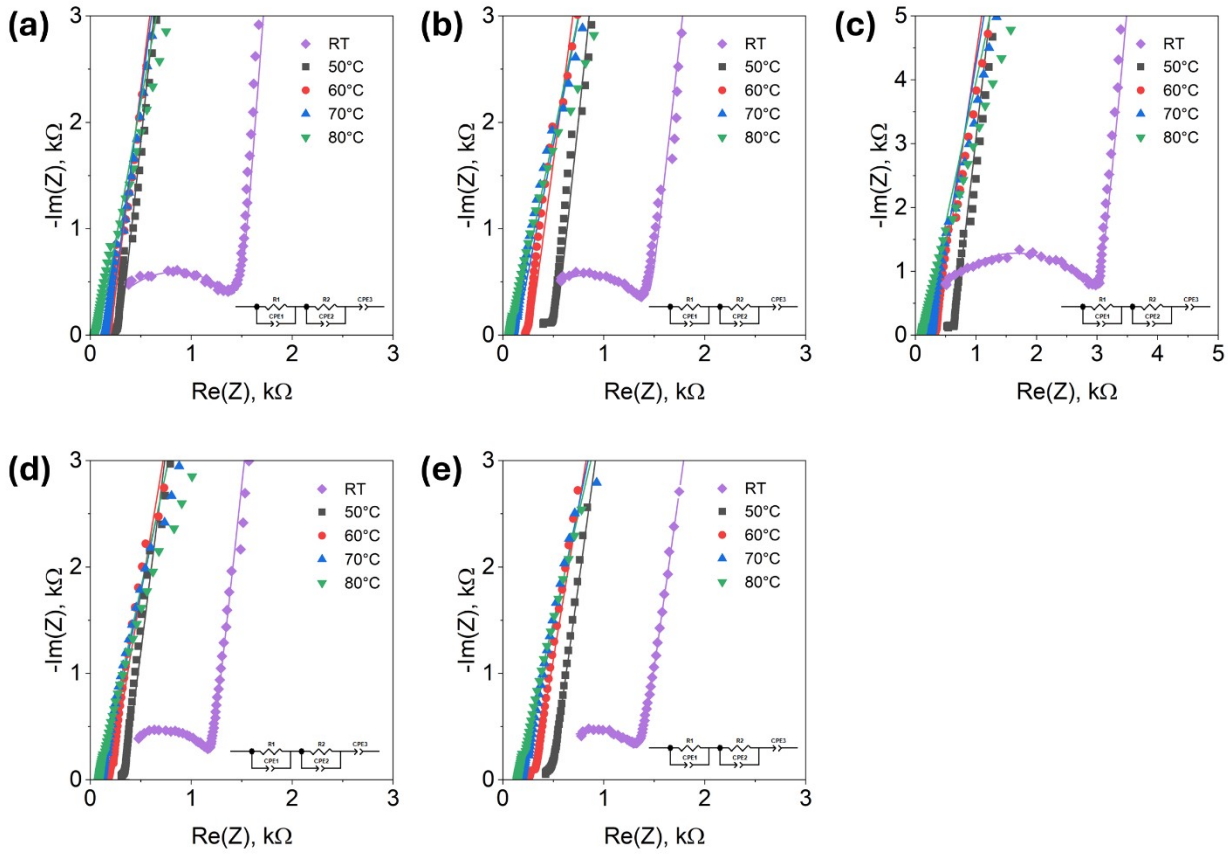

Figure S6. Temperature-dependent impedance spectra and Arrhenius analysis of Li-site doped LLZNTH garnets. (a-e) Nyquist plots collected from room temperature to 80 °C for (a) Al0.2, (b) Fe0.2, (c) Ga0.2, (d) Zn0.2, and (e) Fe0.1.

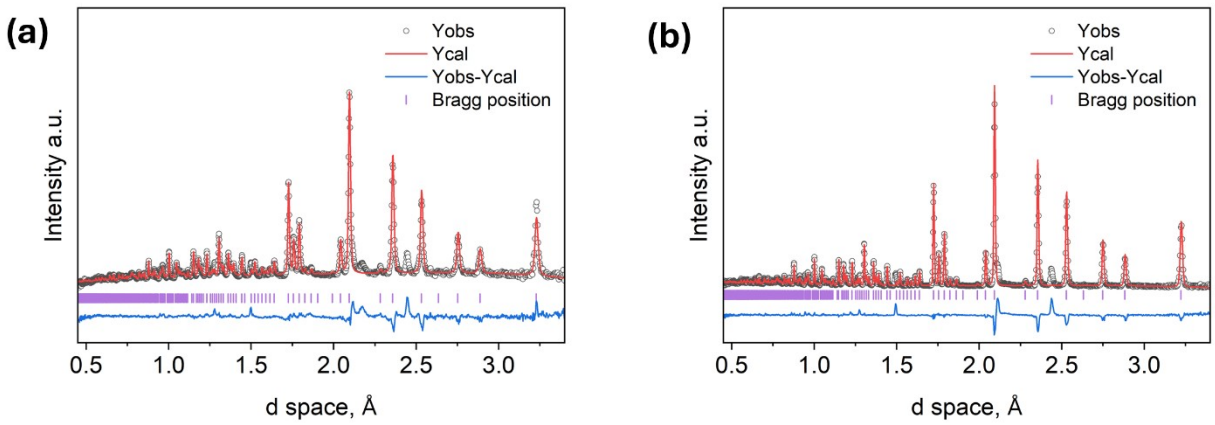

Figure S7. Neutron diffraction Rietveld refinement profiles of LLZNTH samples with different Li-site dopants: (a) Al0.1, (b) Fe0.1

Table S1. A summary of the Rietveld refinement results

Sample	Lattice parameter (nm)	Rwp (%)	GOF	Site	Occupancy	x	y	z	Uiso (Å²)
$Li_6La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$	1.289736(1)	5.96	13.62	Li1(96h)	0.4049	0.6524	0.1729	0.0643	3.4
				Li2(24d)	0.5444	0.25	0.375	0	4
				La(24c)	1	0.25	0.125	0	1
				Zr(16a)	0.25	0	0	0	0.9
				Nb(16a)	0.25	0	0	0	0.9
				Ta(16a)	0.25	0	0	0	0.9
				Hf(16a)	0.25	0	0	0	0.9
				O(96h)	1	0.0527	0.1471	-0.031	1.4
$Li_{5.4}Al_{0.2}La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$	1.288853(1)	4.77	9.27	Li1(96h)	0.3195	0.6481	0.1726	0.0615	1.1
				Li2(24d)	0.8001	0.25	0.375	0	4.1
				Al(24d)	0.0666	0.25	0.375	0	4
				La(24c)	1	0.25	0.125	0	1
				Zr(16a)	0.25	0	0	0	0.9
				Nb(16a)	0.25	0	0	0	0.9
				Ta(16a)	0.25	0	0	0	0.9
				Hf(16a)	0.25	0	0	0	0.9
				O(96h)	1	0.0527	0.1469	-0.0304	1.4
$Li_{5.4}Fe_{0.2}La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$	1.288668(1)	7.73	22.56	Li1(96h)	0.2864	0.6598	0.1623	0.0618	2.6
				Li2(24d)	0.8379	0.25	0.375	0	3.3
				Fe(24d)	0.0615	0.25	0.375	0	3.2

				La(24c)	1	0.25	0.125	0	1
				Zr(16a)	0.25	0	0	0	0.9
				Nb(16a)	0.25	0	0	0	0.9
				Ta(16a)	0.25	0	0	0	0.9
				Hf(16a)	0.25	0	0	0	0.9
				O(96h)	1	0.0527	0.1469	-0.0308	1.4
$Li_{5.6}Zn_{0.2}La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$	1.290450(1)	6.03	16.6	Li1(96h)	0.3293	0.6539	0.1648	0.051	2.1
				Li2(24d)	0.8667	0.25	0.375	0	4
				Zn(24d)	0.0759	0.25	0.375	0	0.5
				La(24c)	1	0.25	0.125	0	1
				Zr(16a)	0.25	0	0	0	0.9
				Nb(16a)	0.25	0	0	0	0.9
				Ta(16a)	0.25	0	0	0	0.9
				Hf(16a)	0.25	0	0	0	0.9
				O(96h)	1	0.0531	0.1472	-0.0309	1.4
$Li_{5.4}Ga_{0.2}La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$	1.2885604(1)	5.59	13.78	Li1(96h)	0.2983	0.6493	0.1702	0.06	3.4
				Li2(24d)	0.7998	0.25	0.375	0	4.8
				Ga(24d)	0.0697	0.25	0.375	0	4
				La(24c)	1	0.25	0.125	0	1
				Zr(16a)	0.25	0	0	0	0.9
				Nb(16a)	0.25	0	0	0	0.9
				Ta(16a)	0.25	0	0	0	0.9

				Hf(16a)	0.25	0	0	0	0.9
				O(96h)	1	0.0523	0.1465	-0.0306	1.4