The role of aliovalent dopants on the structural and transport properties of $Li_6La_2BaTa_2O_{12}$ garnet Li-ion solid electrolyte

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Table S1: Extracted atomic parameters from Rietveld refinement of the $Li_6BaLa_2Ta_2O_{12}$ PXRD. Refined *a* = 13.0018(1) Å.

Atom	x	y	z	Uiso (100/Å^2)	Site	Frac.
Li1	3/8	0	1/4	2.43	24d	0.300
Li2	0.1456	0.656485	0.56	2.41	96h	0.420
Ba1	1/8	0	1/4	2.34(4)	24c	0.330(3)
La1	1/8	0	1/4	2.34(4)	24c	0.666
Ta1	0	0	0	2.34(4)	16a	1.000
O1	-0.0355(4)	0.0473(5)	0.1456(4)	2.35(4)	96h	1.000

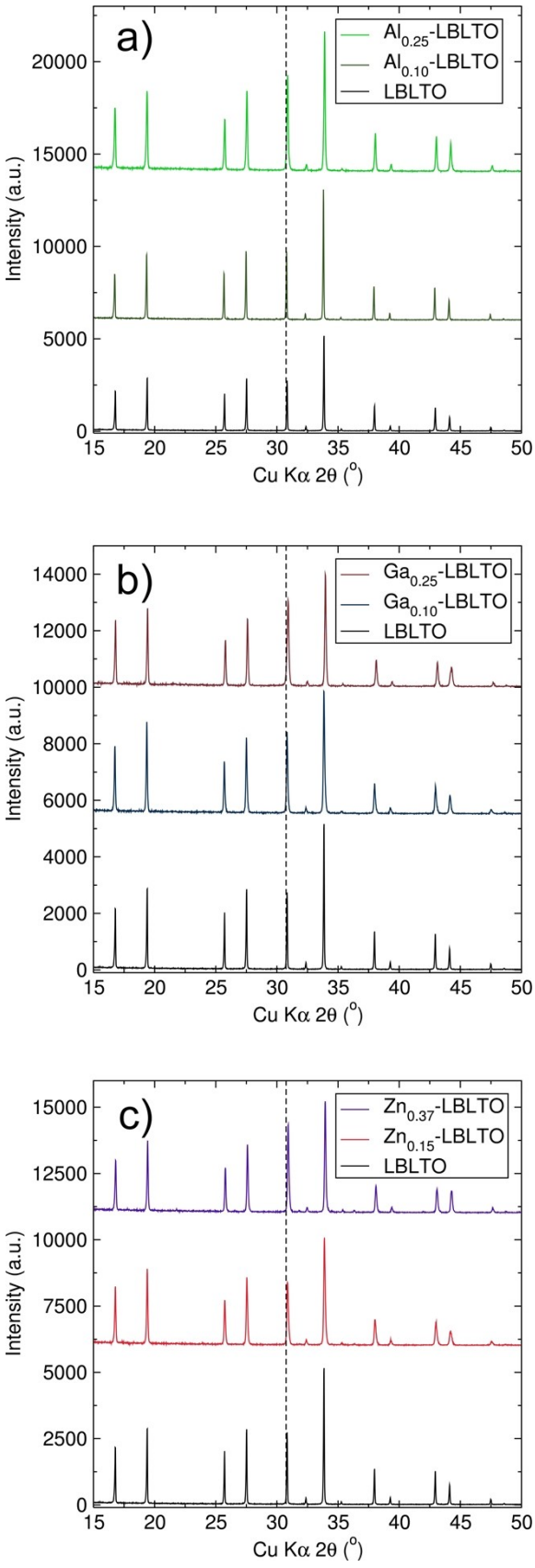

Figure S1: PXRD patterns collected from the (a) Al-doped $Li_{6-3x}Al_xBaLa_2Ta_2O_{12}$ (Al_x-LBLTO), (b) Ga-doped $Li_{6-3x}Ga_xBaLa_2Ta_2O_{12}$ (Ga_x-LBLTO) and (c) Zn-doped $Li_{6-2x}Zn_xBaLa_2Ta_2O_{12}$ (Zn_xLBLTO) materials. The dotted line indicates (402) Bragg reflection.

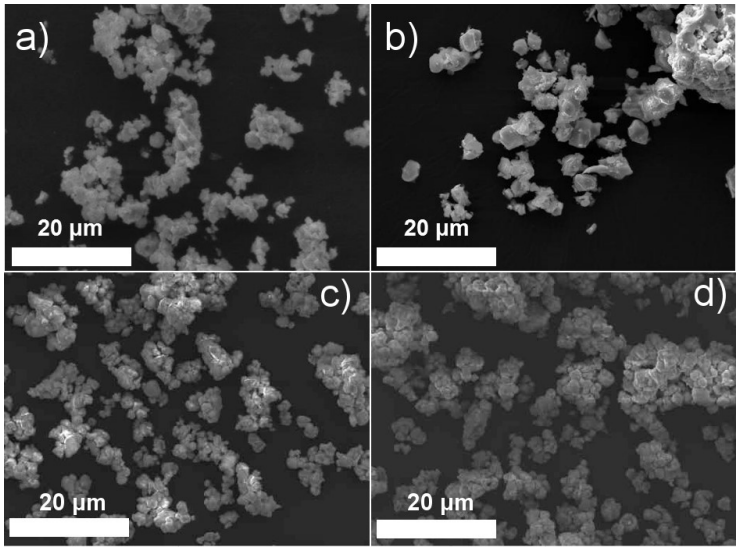

Figure S2: SEM images of the (a) undoped $Li_6BaLa_2Ta_2O_{12}$, (b) $Li_{5.25}Al_{0.25}BaLa_2Ta_2O_{12}$, (c) $Li_{5.25}Ga_{0.25}BaLa_2Ta_2O_{12}$ and (d) $Li_{5.25}Zn_{0.37}BaLa_2Ta_2O_{12}$ garnet materials.

Table S2: Atomic concentration of the different metals present in the $Li_6BaLa_2Ta_2O_{12}$, $Li_{5.25}Al_{0.25}BaLa_2Ta_2O_{12}$ ($Al_{0.25}$LBLTO), $Li_{5.25}Ga_{0.25}BaLa_2Ta_2O_{12}$ ($Ga_{0.25}$LBLTO) and $Li_{5.25}Zn_{0.37}BaLa_2Ta_2O_{12}$ ($Zn_{0.37}$LBLTO) materials as obtained from EDX measurements.

Metal	LBLTO	$Al_{0.25}$LBLTO	$Ga_{0.25}$LBLTO	$Zn_{0.37}$LBLTO
Al	-	0.3(3)	-	-
Ga	-	-	0.2(2)	-
Zn	-	-	-	0.2(3)
Ba	1.1(6)	1.3(3)	1.0(2)	0.9(3)
La	2.2(8)	2.8(9)	1.7(5)	2.0(6)
Ta	2.0(3)	2.0(3)	2.0(2)	2.0(3)

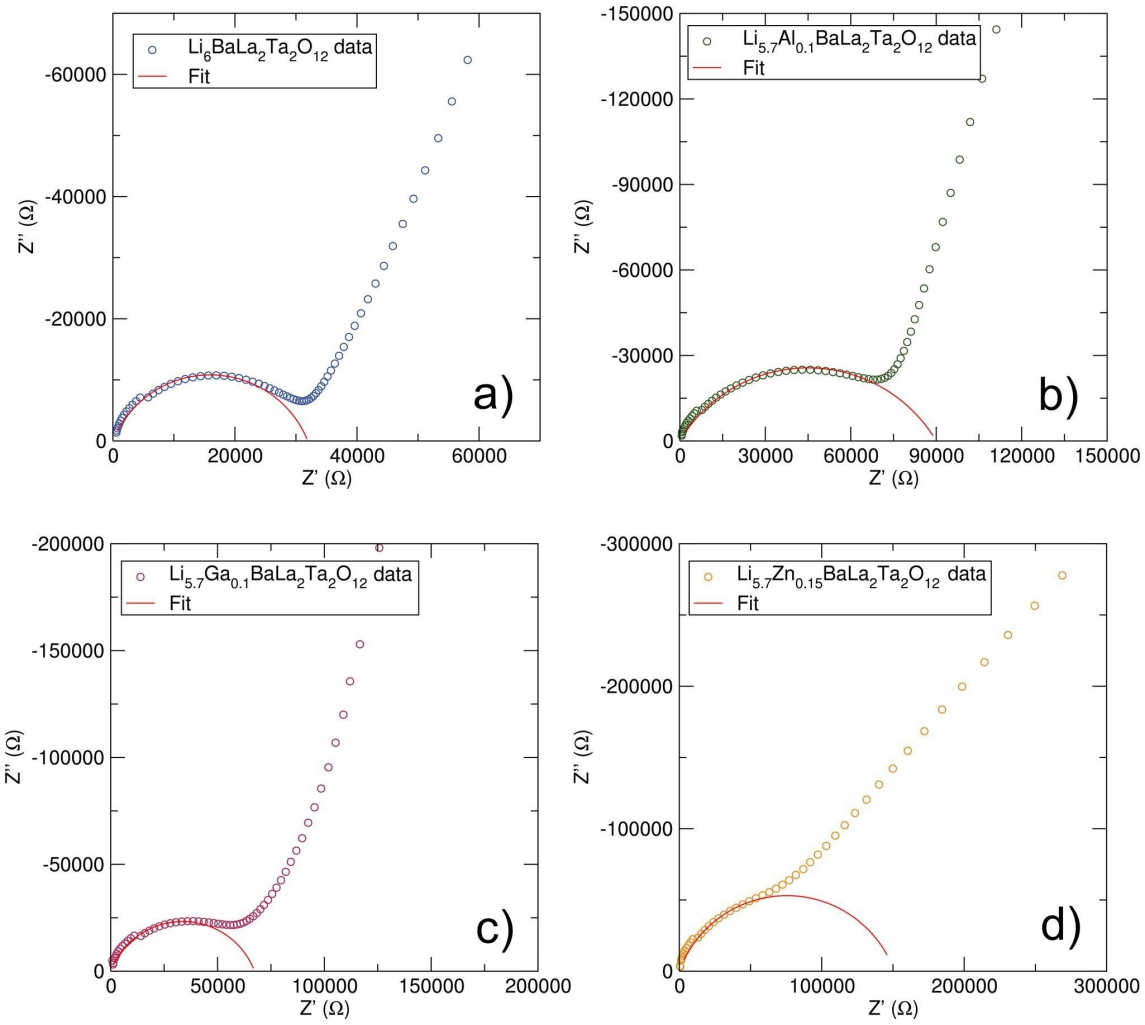

Figure S3: Nyquist plots of the EIS experimental data at room temperature (open circles) and their fit (solid line) to a resistance with a parallel constant phase element.

Table S3: Room temperature ionic conductivity of the undoped and Al-, Ga-, Zn-doped $Li_6BaLa_2Ta_2O_{12}$ materials calculated from EIS measurements.

Material	σ (S cm^{-1})
$Li_6BaLa_2Ta_2O_{12}$	3.7×10^{-6}
$Li_{5.70}Al_{0.10}BaLa_2Ta_2O_{12}$	7.9×10^{-7}
$Li_{5.25}Al_{0.25}BaLa_2Ta_2O_{12}$	2.8×10^{-9}
$Li_{5.70}Ga_{0.10}BaLa_2Ta_2O_{12}$	3.2×10^{-6}
$Li_{5.25}Ga_{0.25}BaLa_2Ta_2O_{12}$	2.6×10^{-6}
$Li_{5.70}Zn_{0.15}BaLa_2Ta_2O_{12}$	1.2×10^{-6}
$Li_{5.25}Zn_{0.37}BaLa_2Ta_2O_{12}$	6.6×10^{-7}

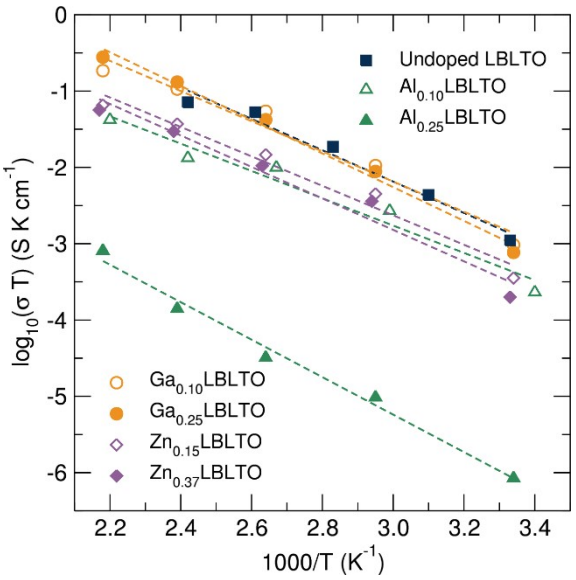

Figure S4: Arrhenius plots of ionic conductivity from EIS measurements for the (a) Al-doped $Li_{6-3x}Al_xBaLa_2Ta_2O_{12}$ (Al_x-LBLTO), (b) Ga-doped $Li_{6-3x}Ga_xBaLa_2Ta_2O_{12}$ (Ga_x-LBLTO) and (c) Zn-doped $Li_{6-2x}Zn_xBaLa_2Ta_2O_{12}$ (Zn_xLBLTO) materials.

Table S4: Activation energy for the total ionic conductivity and the correspondent R^2 from the Arrhenius fits for the undoped and Al^{3+}, Ga^{3+}, Zn^{2+} doped $Li_6BaLa_2Ta_2O_{12}$ materials calculated from EIS measurements.

Material	E_a (eV)	R^2
LBLTO	0.41(4)	0.98
$Li_{5.70}Al_{0.10}BaLa_2Ta_2O_{12}$	0.35(4)	0.96
$Li_{5.25}Al_{0.25}BaLa_2Ta_2O_{12}$	0.48(3)	0.99
$Li_{5.70}Ga_{0.10}BaLa_2Ta_2O_{12}$	0.41(3)	0.98
$Li_{5.25}Ga_{0.25}BaLa_2Ta_2O_{12}$	0.43(1)	0.99
$Li_{5.70}Zn_{0.15}BaLa_2Ta_2O_{12}$	0.38(4)	0.97
$Li_{5.25}Zn_{0.37}BaLa_2Ta_2O_{12}$	0.41(4)	0.97

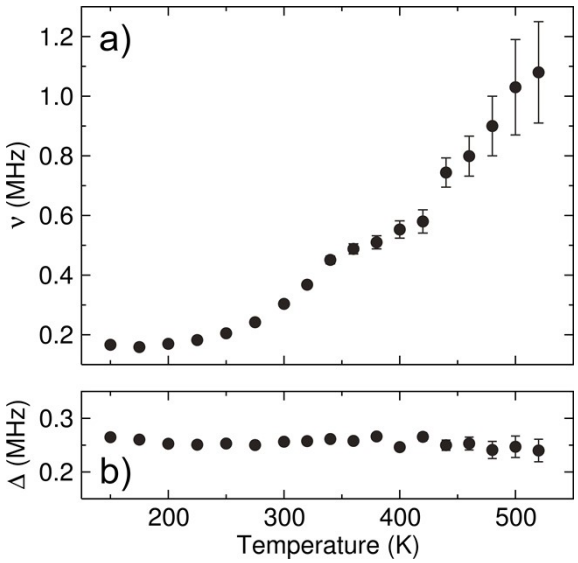

Figure S5: Temperature dependence of (a) ν and (b) Δ values obtained for fits to the Keren function for the undoped $Li_6BaLa_2Ta_2O_{12}$ garnet measured from 150 K to 525 K.

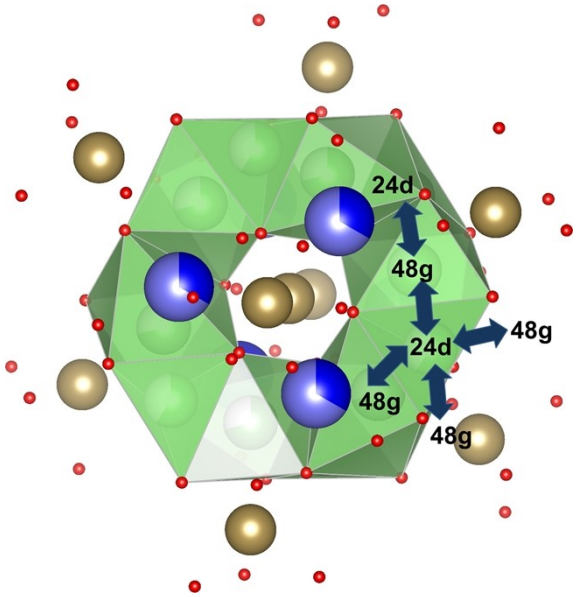

Figure S6: Simplified crystal structure representation of the cubic $LiBaLa_2Ta_2O_{12}$ undoped material, where the diffusion pathways between 24d and 48g sites for Li^+ has been indicated by the blue arrows. Ba^{2+} and La^{3+} cations are shown in blue and purple respectively, Ta^{5+} in brown, O^{2-} anions in red and Li^+ ion in green enclosed in their coordination polyhedra.