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

Competition between activation energy and migration entropy in lithium ion conduction in superionic NASICON-type $Li_{1-3x}Ga_xZr_2(PO_4)_3$

Supporting information

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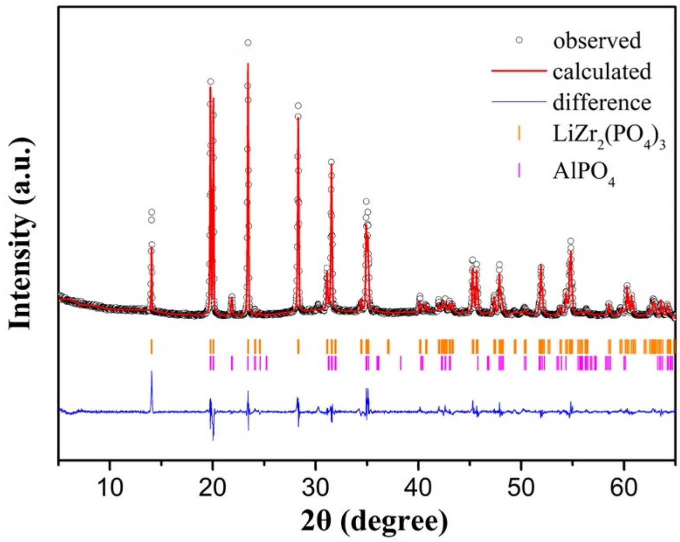

Figure S1 Rietveld refinement of $LiZr_2(PO_4)_3$, experimental data are shown as points; the red line denotes the calculated pattern; and the difference profile is shown in blue.

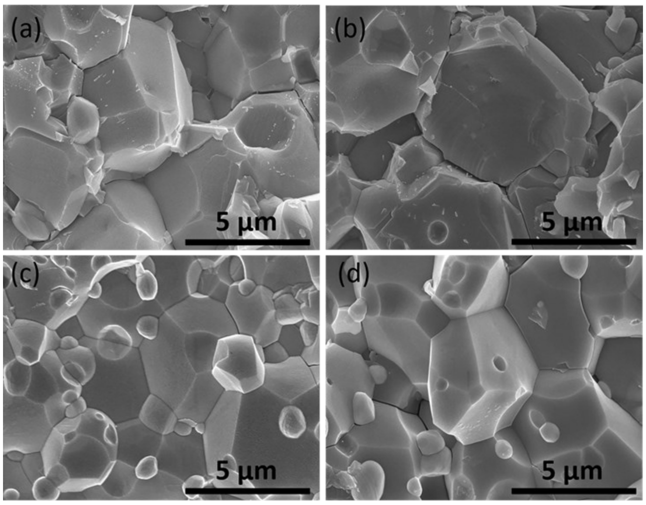

Figure S2 SEM images of (a) $LiZr_2(PO_4)_3$, (b) $Li_{0.94}Ga_{0.02}Zr_2(PO_4)_3$, (c) $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$ and (d) $Li_{0.7}Ga_{0.1}Zr_2(PO_4)_3$

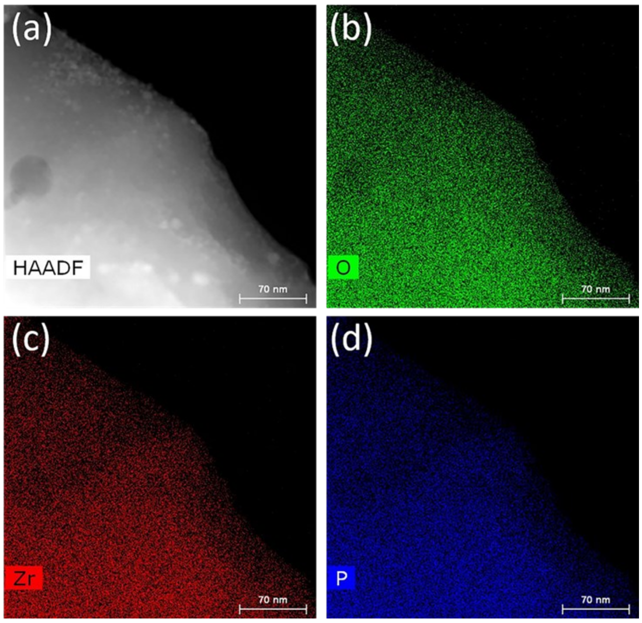

Figure S3 (a) HAADF image and corresponding (b) O, (c) Zr, (d) P element mappings of $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$

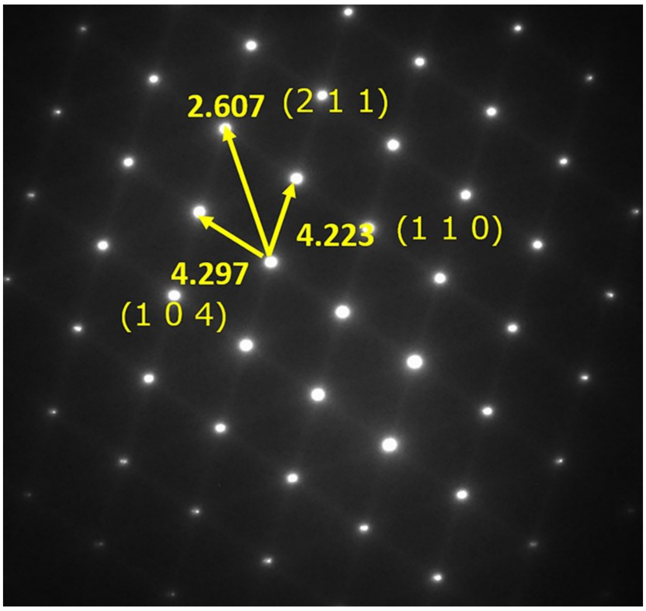

Figure S4 Selected area electron diffraction pattern of $LiZr_2(PO_4)_3$.

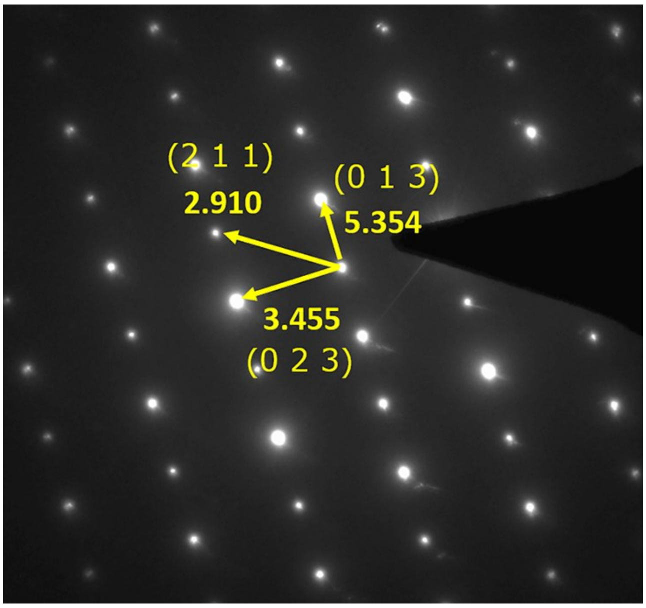

Figure S5 Selected area electron diffraction pattern of $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$.

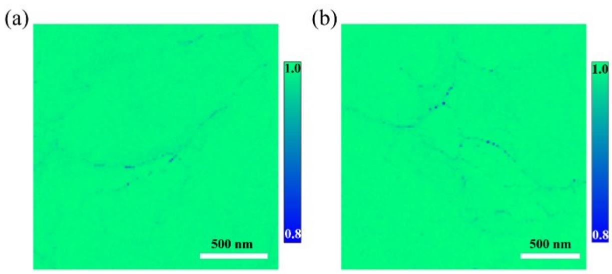

Figure S6 R^2 mappings of (a) $LiZr_2(PO_4)_3$ and (b) $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$.

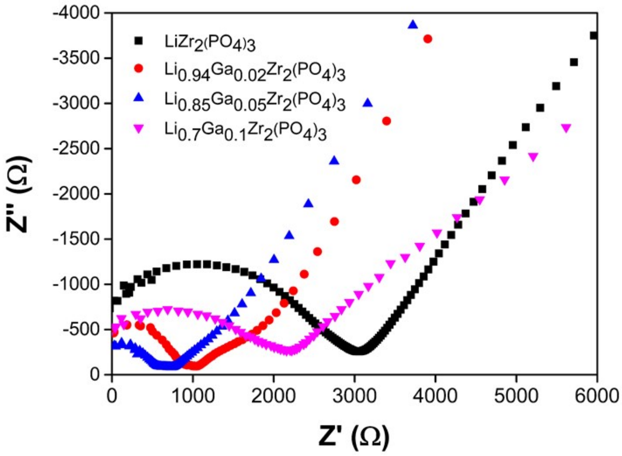

Figure S7 Complex impedance plots measured at room temperature for $LiZr_2(PO_4)_3$, $Li_{0.94}Ga_{0.02}Zr_2(PO_4)_3$, $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$ and $Li_{0.7}Ga_{0.1}Zr_2(PO_4)_3$.

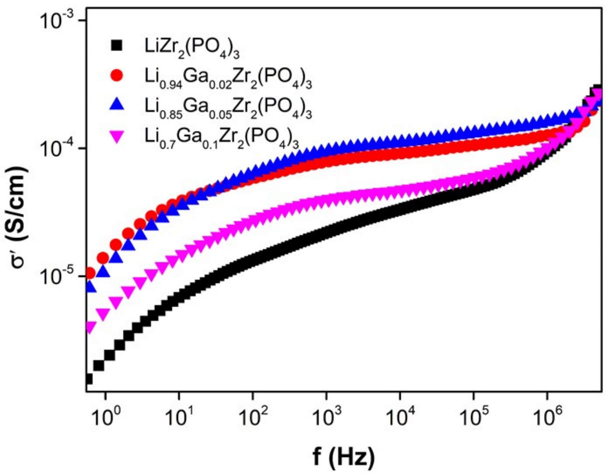

Figure S8 Frequency-dependent ionic conductivity of the $Li_{1-3x}Ga_xZr_2(PO_4)_3$ (x=0, 0.02, 0.05, 0.1) samples.

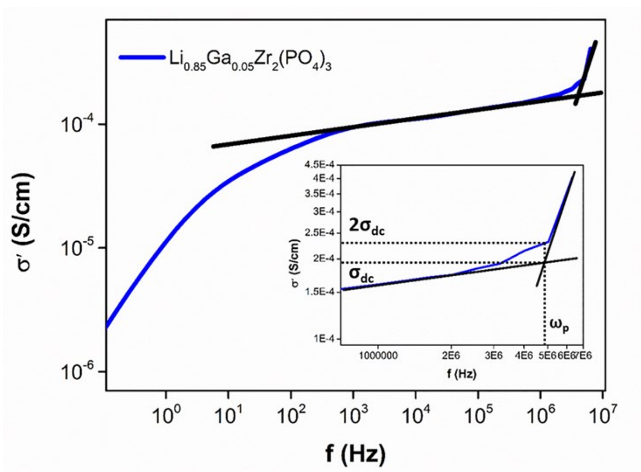

Figure S9 A method of estimating jump frequency from $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$ a.c. conductivity data. The insert represents a larger version in high frequency.

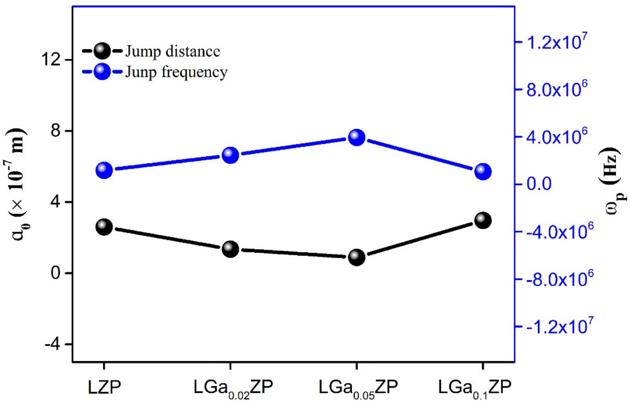

Figure S10 Compositional dependence of the jump distance and jump frequency of the $Li_{1-3x}Ga_xZr_2(PO_4)_3$ (x=0, 0.02, 0.05, 0.1) samples. Straight lines through data points are guides for the eye.

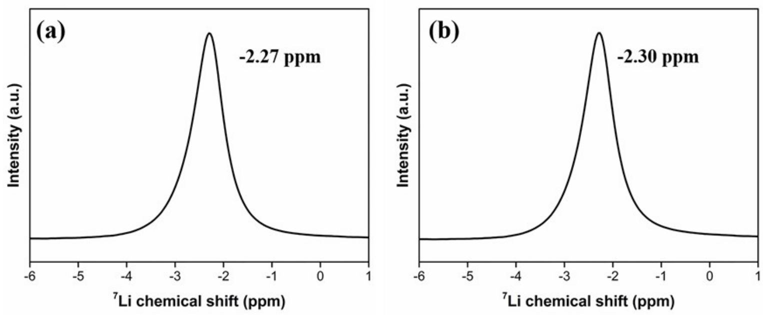

Figure S11 ^{7}Li MAS-NMR spectra of (a) $LiZr_2(PO_4)_3$ and (b) $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$.

Table S1 Comparison of chemical analysis between $LiZr_2(PO_4)_3$, $Li_{0.94}Ga_{0.02}Zr_2(PO_4)_3$, $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$ and $Li_{0.7}Ga_{0.1}Zr_2(PO_4)_3$ by ICP-OES

Sample	Li (wt.%)	Zr (wt.%)	P (wt.%)	Ga (wt.%)	Al (wt.%)
$LiZr_2(PO_4)_3$	1.38	37.7	19.9	\	0.613
$Li_{0.94}Ga_{0.02}Zr_2(PO_4)_3$	1.27	37.2	19.4	0.251	0.529
$Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$	1.11	36.5	18.8	0.683	0.507
$Li_{0.7}Ga_{0.1}Zr_2(PO_4)_3$	0.945	36.7	19.2	1.36	0.563

Table S2 Rietveld refinements for $LiZr_2(PO_4)_3$ and $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$

Sample	$LiZr_2(PO_4)_3$	$Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$
R_p	8.22%	7.52%
a, Å	8.8473	8.8541
c, Å	22.1636	22.1458
V, Å^3	1502.441	1503.526

<P-O1>, Å	1.4366(2)	1.4169(2)
<P-O2>, Å	1.5395(2)	1.4990(2)
<Zr-O1>, Å	2.1015(3)	2.1714(3)
<Zr-O2>, Å	2.0385(3)	2.0627(3)

Table S3 CPE_1, R_1, CPE_2, R_2 and W fitting values for $LiZr_2(PO_4)_3$, $Li_{0.94}Ga_{0.02}Zr_2(PO_4)_3$, $Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$ and $Li_{0.7}Ga_{0.1}Zr_2(PO_4)_3$

Sample	CPE_1	R_1	CPE_2	R_2	W
$LiZr_2(PO_4)_3$	119.8 pF	2302 Ω	29.81 nF	826.3 Ω	43.15 Ω $S^{-1/2}$
$Li_{0.94}Ga_{0.02}Zr_2(PO_4)_3$	19.04 pF	578.3 Ω	1.224nF	354.5 Ω	15.27 Ω $S^{-1/2}$
$Li_{0.85}Ga_{0.05}Zr_2(PO_4)_3$	10.94 pF	193.7 Ω	1.061 nF	367.5 Ω	16.58 Ω $S^{-1/2}$
$Li_{0.7}Ga_{0.1}Zr_2(PO_4)_3$	53.24 pF	1341 Ω	3.478 nF	746.2 Ω	35.53 Ω $S^{-1/2}$