Supporting Information.

Polymorphism in $Li_4Zn(PO_4)_2$ and stabilization of its structural disorder to improve ionic conductivity

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Direct Current (DC) Polarization measurement.

The electronic conductivity was determined by the DC polarization method to differentiate electronic contribution to the ionic conductivity. The β'-$Li_{3.5}Zn_{0.5}Ga_{0.5}(PO_4)_2$ sample was chosen as a representative for the measurement. DC voltages of 1, 1.25, and 1.5 V were applied to the sample pellet placed between two Pt electrodes prior to reach steady-state over 20 mins. The resistance was then obtained using Ohm's law and the results are summarized in Figure S9. The electronic conductivity at room temperature was obtained by extrapolation of the Arrhenius plot, and leads to a value of ~$1.2 \cdot 10^{-16}$ $S \cdot cm^{-1}$, which is three orders of magnitude lower than the ionic conductivity at RT measured by AC Impedance spectra. This demonstrated that the electronic contribution can be neglected and the transference number of Li^+ ions in the $Li_{3.5}Zn_{0.5}Ga_{0.5}(PO_4)_2$ electrolytes is approximately unity.

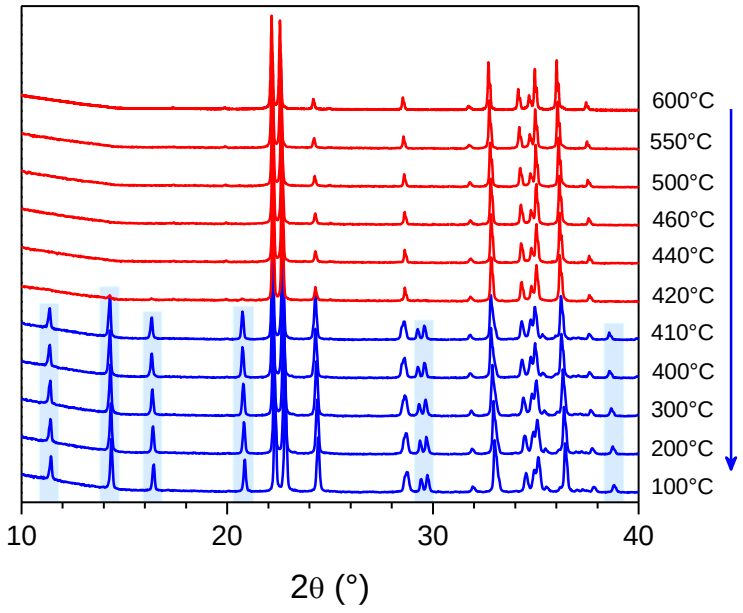

Figure S1. Evolution of XRD patterns of $Li_4Zn(PO_4)_2$ with temperature during cooling. Values of temperatures corresponding to the patterns are indicated at the right. The patterns colored in blue and red corresponds to the α- and β- polymorphs, respectively, and the peaks that reappear for the α- phase has been indicated by blue backgrounds.

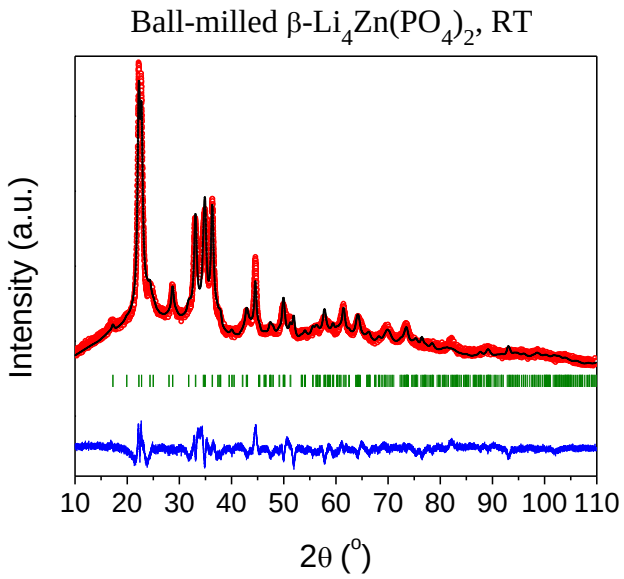

Figure S2. Rietveld refinement of the XRD pattern of the ball-milled β-$Li_4Zn(PO_4)_2$ sample, measured at room temperature. The red circles, black continuous line, blue line and green tick bars represent the observed, calculated, and difference patterns, and Bragg positions, respectively.

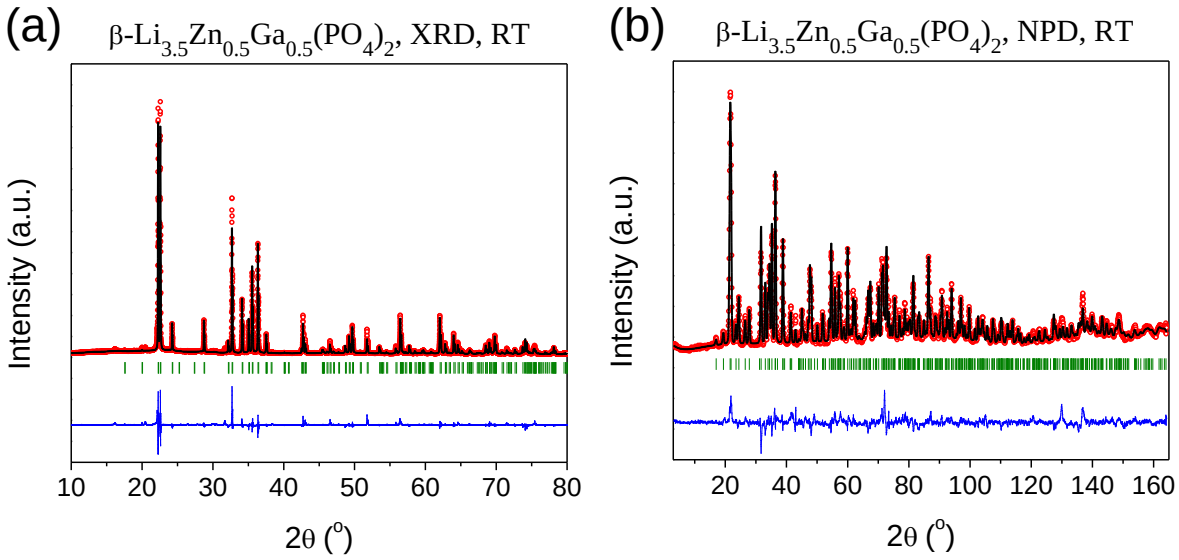

Figure S3. Rietveld refinement of the room temperature XRD (a), and NPD (b) patterns of β-$Li_{3.5}Zn_{0.5}Ga_{0.5}(PO_4)_2$. The red circles, black continuous line, blue line and green tick bars represent the observed, calculated, and difference patterns, and Bragg positions, respectively.

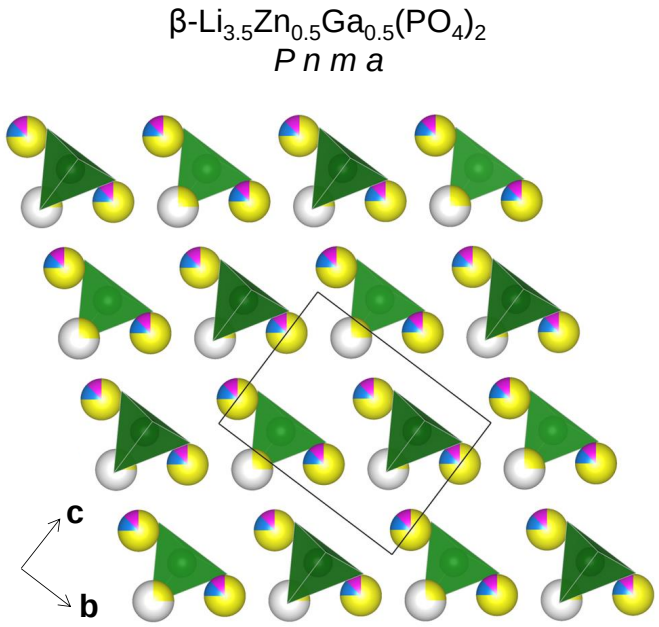

Figure S4. Crystal structure of β-$Li_{3.5}Zn_{0.5}Ga_{0.5}(PO_4)_2$, the unit cell is shown in black parallelogram. For sake of clarity, only half of the unit cell content ($0 \le y \le ½$ in the monoclinic setting) is shown. Li, Zn and Ga are shown in blue, yellow and pink, respectively and PO_4 tetrahedra are colored in green.

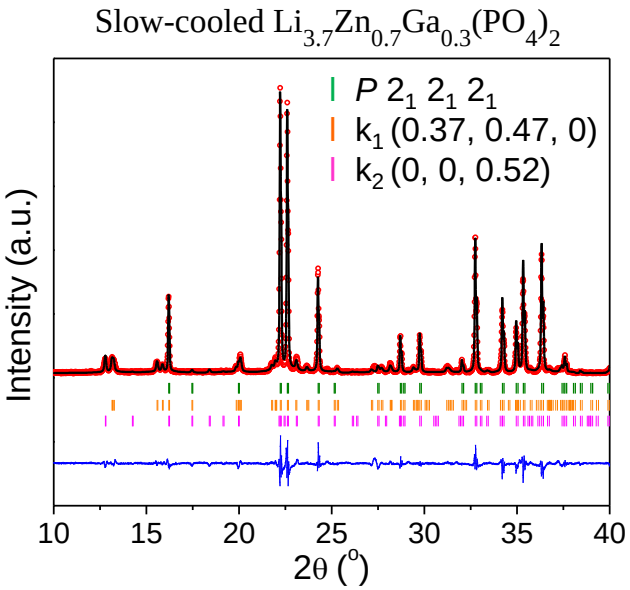

Figure S5. Rietveld refinement of the room temperature XRD pattern of sc-$Li_{3.7}Zn_{0.7}Ga_{0.3}(PO_4)_2$ using the *P* 2_1 2_1 2_1 unit cell and $\mathbf{k_1}$ and $\mathbf{k_2}$ propagation vectors. The red circles, black continuous line, blue line and represent the observed, calculated, and difference patterns, respectively. Tick bars represent the Bragg positions of the respective phases as indicated in the legends.

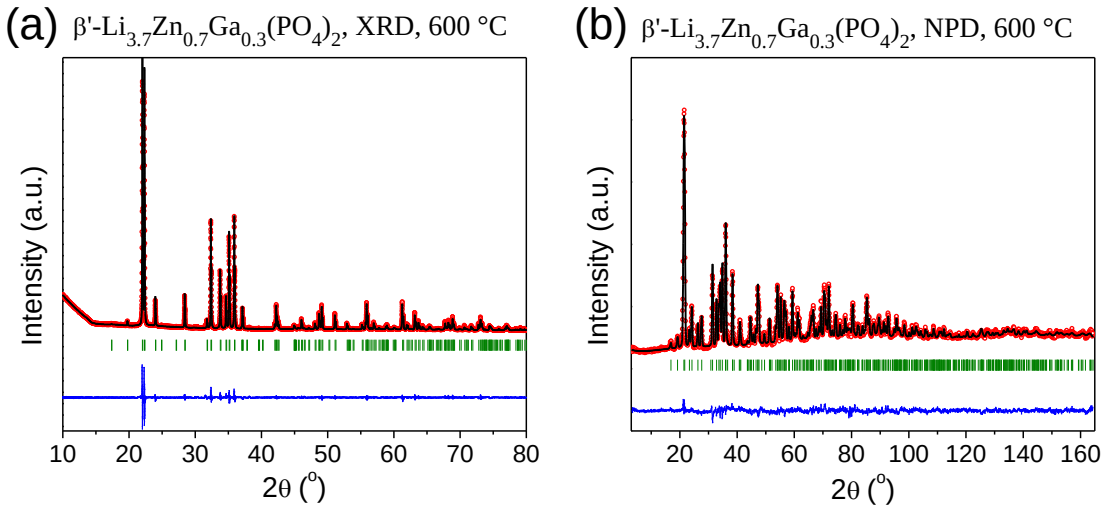

Figure S6. Rietveld refinement of the XRD (a), and NPD (b) patterns of β'-$Li_{3.7}Zn_{0.7}Ga_{0.3}(PO_4)_2$ at 600 °C. The red circles, black continuous line, blue line and green tick bars represent the observed, calculated, and difference patterns, and Bragg positions, respectively.

Table S1. Structural Parameters for β-$Li_{3.7}Zn_{0.7}Ga_{0.3}(PO_4)_2$ deduced from the combined Rietveld refinement of the XRD and neutron patterns recorded at 600 °C.

β-$Li_{3.7}Zn_{0.7}Ga_{0.3}(PO_4)_2$, 600 °C Space group *P n m a* *a* = 10.20903(3) Å, *b* = 6.57170(2) Å, *c* = 4.996639(16) Å, *V* = 333.66(6) Å^3, *Z* = 2						
atom	site	x	y	z	B_{iso}	Occupancy
P1	4*c*	0.40749(13)	0.75	0.8135(3)	2.01(6)	1
O1	8*d*	0.34021(19)	0.5588(2)	0.6975(4)	2.99(5)	1
O2	4*c*	0.5519(2)	0.75	0.7386(5)	2.99(5)	1
O4	4*c*	0.6100(2)	0.25	0.8821(4)	2.99(5)	1
Li1/Zn1/Ga1	8d	0.15404(19)	0.5003(2)	0.8062(4)	3.34(8)	0.750/0.175/0.075
Li3	4c	0.922(3)	0.25	0.781(6)	7.4(9)	0.35

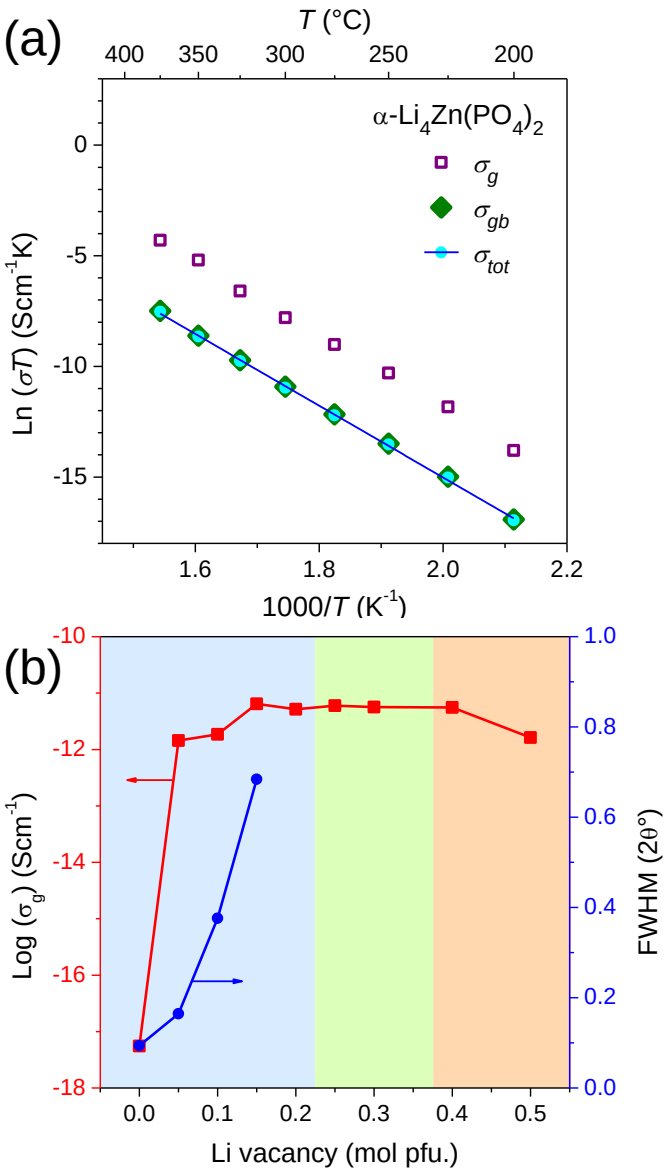

Figure S7. (a) Ionic conductivity of α- $Li_4Zn(PO_4)_2$ sample. (b) Variation of ionic conductivity and broadening of XRD peak with concentration of Li vacancy. The (100) peak of the XRD pattern at 2θ= 16.3° was chosen to estimate the FWHM. The light blue, green and red background represent α-, β'-, and β- polymorphs, respectively.

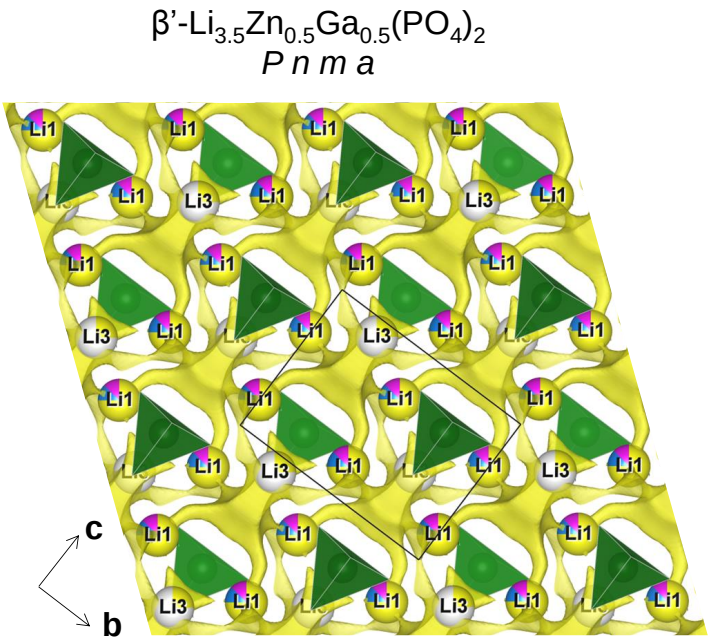

Figure S8. BVEL of β-$Li_{3.5}Zn_{0.5}Ga_{0.5}(PO_4)_2$, at the percolation energies. The yellow domains indicate the migration paths for Li^+ in the structure, obtained using an iso-surface value of 1.1 eV above the minimum energy. For color codes refer to Figure S3.

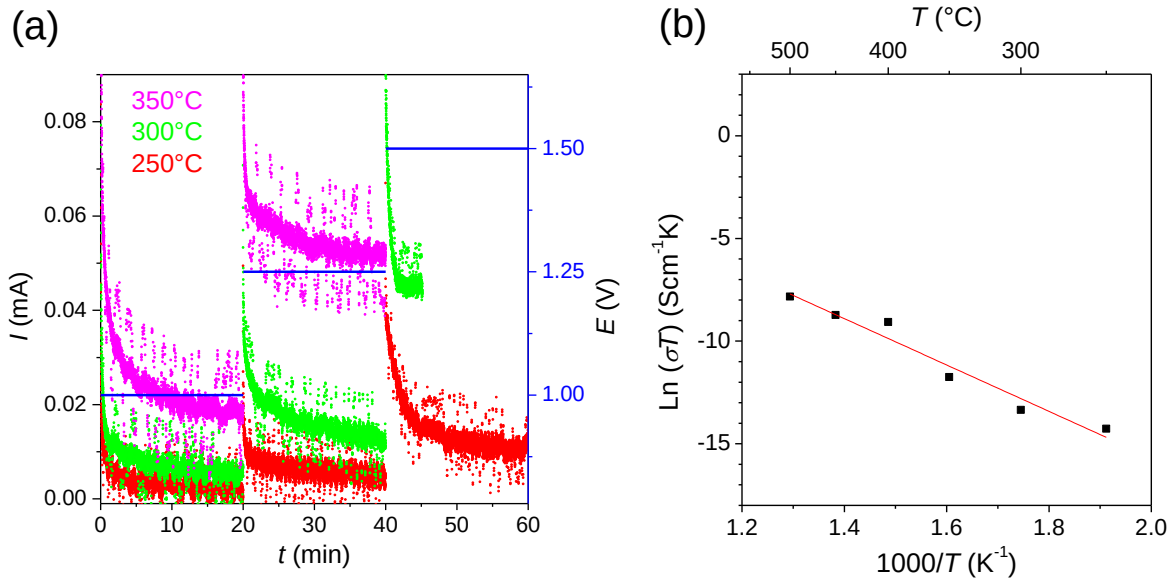

Figure S9. (a) DC polarization plots of β'-$Li_{3.7}Zn_{0.7}Ga_{0.3}(PO_4)_2$ sample at different potentials and temperatures. (b) Arrhenius plot of DC conductivity of the sample.