Supporting Information for

Li^+ /Na^+ Hybrid Ion Conduction Mechanism in the Superionic Conductor $Li_{3-x}Na_xZr_2Si_2PO_{12}$

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Dedication

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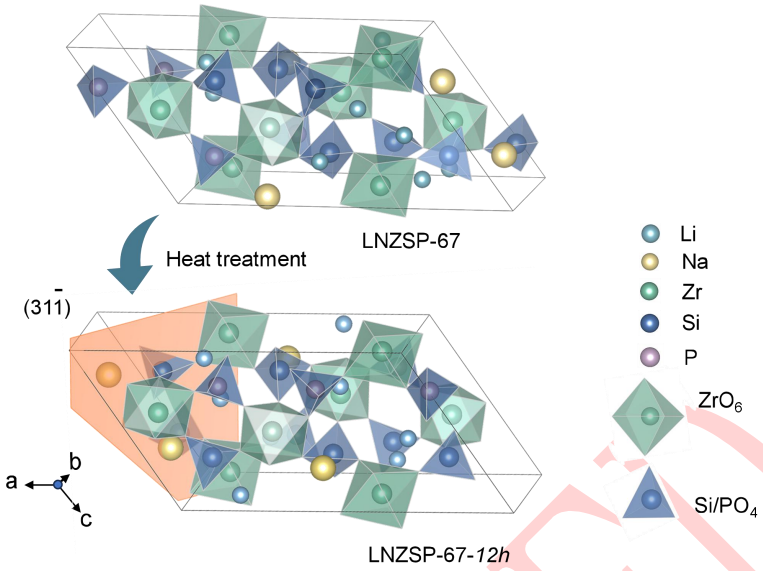

Figure S1. Crystal structure evolution from LNZSP-67 to LNZSP-67-*12h*, with the inset showing the facet corresponding to the diffraction peak at 19.6°.

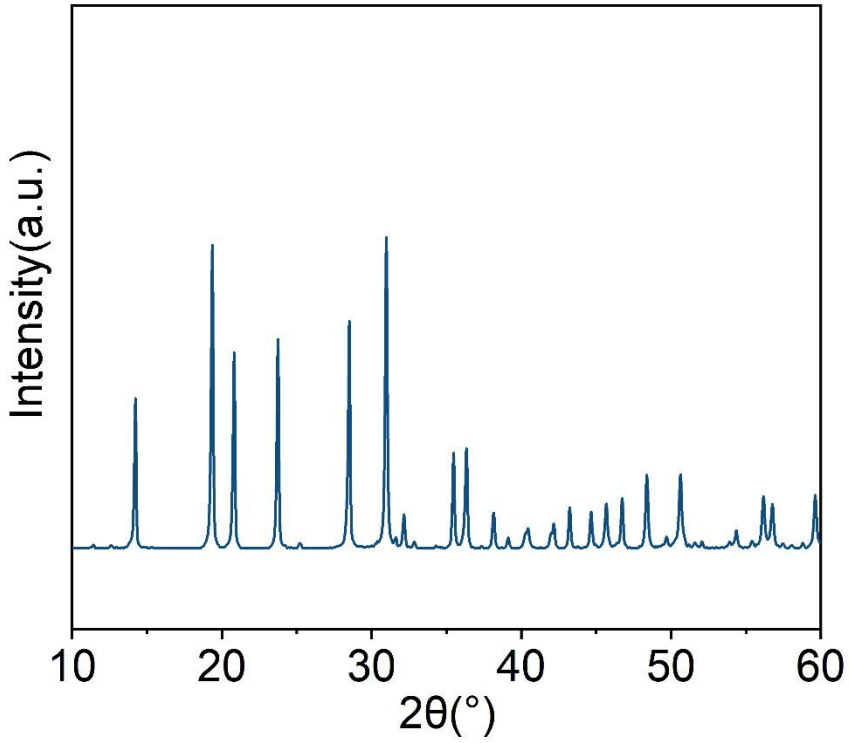

Figure S2. XRD pattern of LNZSP-67-re after subsequent thermal treatment.

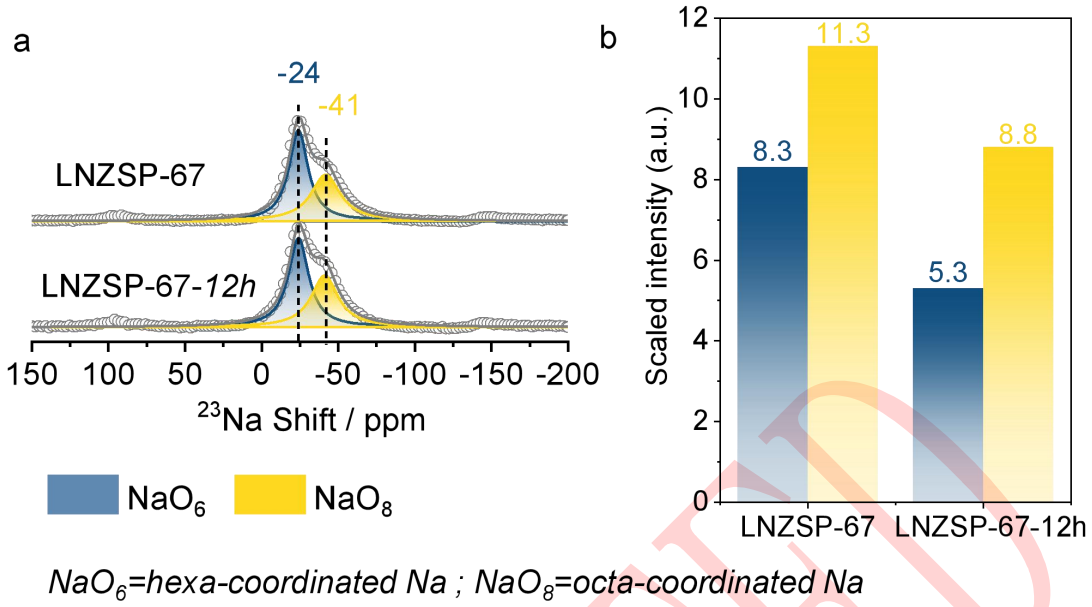

Figure S3. Deconvolution of ^{23}Na ssNMR spectra of LNZSP-67 and LNZSP-67-*12h*. (a) Deconvoluted spectra. (b) Quantified peak intensities for the resonances at -24 and -41 ppm, respectively.

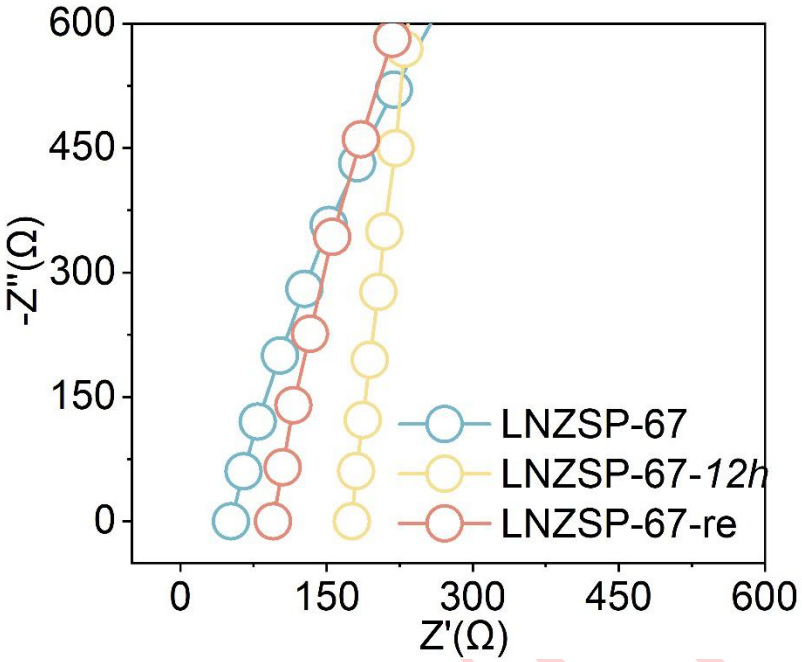

Fig. S4. Enlarged-scale Nyquist plots of LNZSP-67, LNZSP-67-*12h*, and LNZSP-67-re.

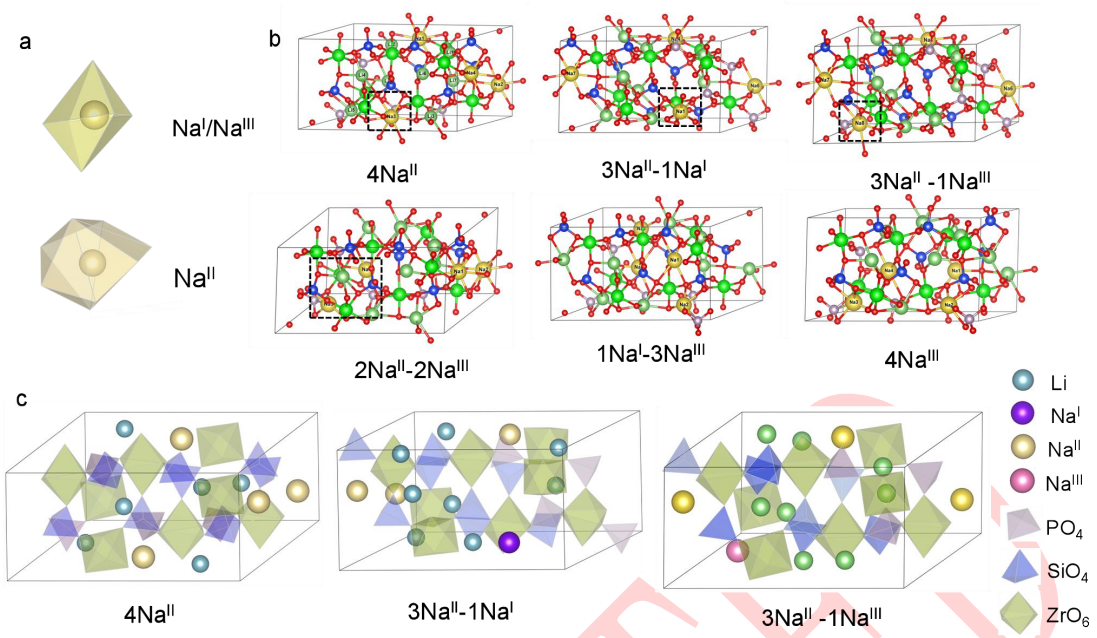

Fig. S5. Enumerated residual-Na configurations and their relative thermodynamic stability in LNZSP-67. (a) Schematic diagrams of Na^{I}, Na^{II}, and Na^{III} sites. (b) Atomic structures of $Na_{12}Zr_8Si_8P_4O_{48}$ configurations (~67%) with different allocations of the four residual Na atoms among the three crystallographic Na sites ($Na^{I}/Na^{II}/Na^{III}$). (c) Corresponding framework–polyhedra views highlighting the NASICON skeleton (ZrO_6, SiO_4, and PO_4) and the spatial distributions of Li and residual Na for selected configurations (e.g., $4Na^{II}$, $3Na^{II}$–$1Na^{I}$, and $3Na^{II}$–$1Na^{III}$).

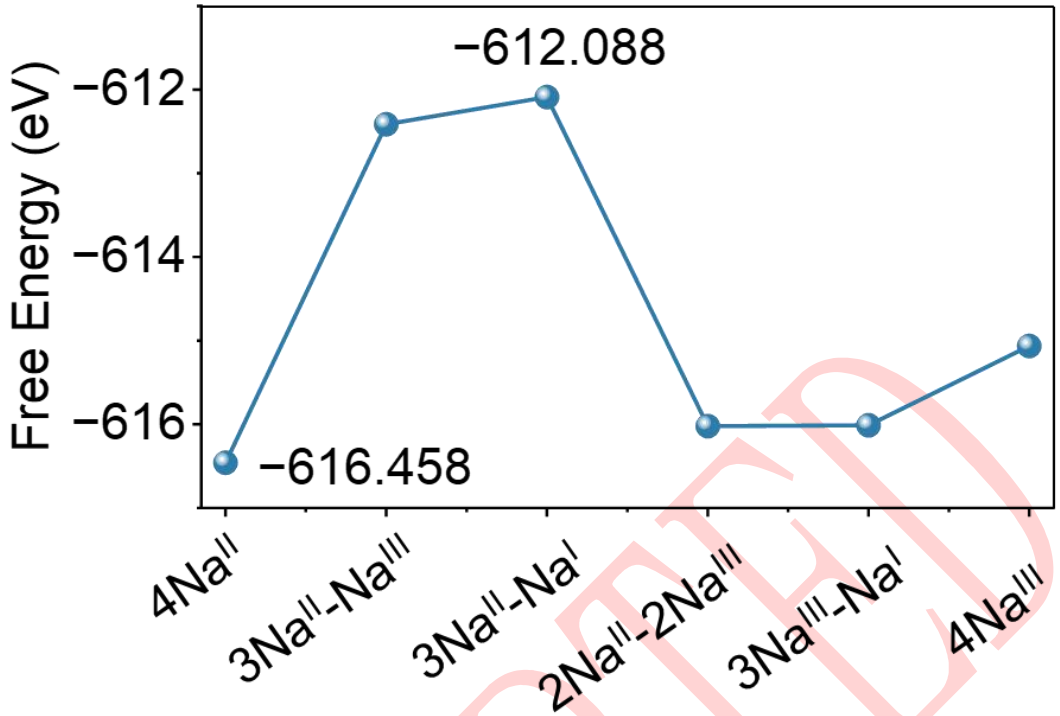

Fig. S6. Relative free energies after full DFT relaxation for the enumerated configurations, showing a thermodynamic preference for residual Na to concentrate at the high-coordination Na^{II} (NaO_8) sites (lowest-energy $4Na^{II}$ state).

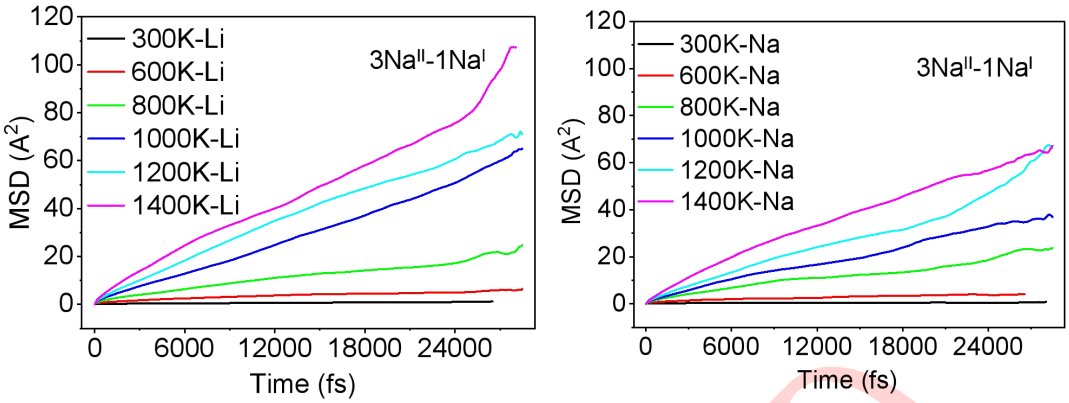

Fig. S7. Mean square displacements (MSDs) of Li^+ (left) and Na^+ (right) for the $3Na^{II}$–$1Na^{I}$ configuration at different temperatures.

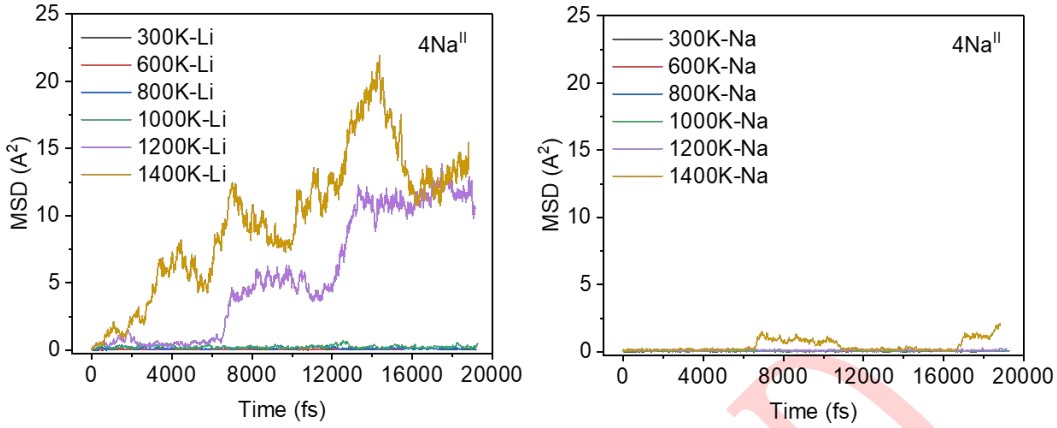

Fig. S8. Mean square displacements (MSDs) of Li^+ (left) and Na^+ (right) for the $4Na^{II}$ configuration at 60 ps.

Table S1. σ_{bulk} and relative density values of LNZSP-67, LNZSP-67-*12h*, and LNZSP-67-re.

	LNZSP-67	LNZSP-67-*12h*	LNZSP-67-re
Relative Density / %	83.75	85.64	84.82
σ_{bulk}/ mS cm^{-1}	1.78	0.50	1.63

Statements & Declarations

Acknowledgements

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Competing Interests

Authors declare no conflict of interest.

Data Availability

All data are available in the main text or the supplementary materials.

Author Contributions

Y.W., X.X., L.Z., M.Y., G.Z., J.C., S.S., Y.W., and W.T. jointly conceived the work. Y.W. performed material synthesis and characterisation. X.X. conducted the DFT calculations. J.C. collected and analysed the NMR spectra. Y.W., X.X., L.Z., M.Y., G.Z., J.C., S.S., Y.W., and W.T. jointly drafted the manuscript. All authors discussed the experimental content and the final manuscript.

Ethics Approval

Authors declare that no human or animal subjects were involved in this study, and no ethical approval was required.

Consent to Participate

Authors declare that no human subjects were involved in this study.

Consent to Publish

Publication consent has been obtained from all participants.