Supporting Information

Peeking the Glass Phase in the Grain Boundary of $Na_3Zr_2Si_2PO_{12}$ by Gallium Modulation

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Experimental Section/Methods

Materials Synthesis: NASICON samples $Na_3Zr_2Si_2PO_{12}$-xGa (x=0-0.2) (NZSP-xGa) were prepared by a conventional solid-state reaction. According to the stoichiometry, Na_2CO_3 (AR, 99.5%, Macklin), ZrO_2 (99.99%, Macklin), Ga_2O_3 (99.99%, Macklin), SiO_2 (99%, Macklin) and $NH_4H_2PO_4$ (99.99%, Macklin) were weighed and mixed. To compensate for the volatile loss of Na, about 10 wt% excess Na_2CO_3 was added to the initial mixture. The powders were ball-milled (ZrO_2 containers and balls) with isopropanol at 600 rpm for 12 h and dried at 60 ^oC for 12 h, then calcinated at 900 ^oC for 12 h. The obtained powders were further ball-milled for additional 12 h, followed by pressing into a pellet at 300 MPa, with extra annealing at 1100 ^oC for 24 h in air. All samples were covered with mother powders during sintering.

Materials Characterization: The crystal structure was investigated by powder X-ray diffraction (XRD) with Cu-K radiation (Empyrean PANalytical, Holland; λ=0.154 nm). The microscopy characteristics of samples were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (JSM-7900F and JEM-F200, respectively). The chemical composition of products was studied by EDS (JSM-7900F).

NMR Experiments: All solid state NMR experiments were acquired on a Bruker 600 MHz (14.1 T) magnet with AVANCE NEO consoles using Bruker 3.2 mm HXY magic angle spinning (MAS) probe. The Larmor frequencies for ^{23}Na, ^{31}P were determined as 158.78 MHz and 242.99 MHz, respectively. All spectra were acquired with one-pulse and were referenced to 1 M NaCl solution (0 ppm) and 85% H_3PO_4 solution (0 ppm), respectively. The ^{23}Na and ^{31}P spin−lattice relaxation times (T_1) were recorded using saturation recovery pulse sequence. Recycle delays were set longer than 5 × T_1 for all experiments. The spinning rate ν_{rot} was set to 14 kHz for ^{23}Na and ^{31}P, respectively. The varying temperature experiments were protected by N_2 atomosphere. All spectra were simulated by using ssNake software[45].

Electrochemical Measurements: The ionic conductivity of NZSP-xGa pellets were measured with electrochemical impedance spectroscopy (EIS) (Solartron 1260/1296 frequency response

analyzer). Silver was coated on the pellets by spreading as the blocking electrodes before conductivity measurement. The measured frequency range was 10 MHz to 1 Hz. The temperature dependence of the conductivity was measured in the same way at several specific temperatures ranging from 30 to 110 ^{o}C at a BioLogic electrochemical station (SP-300). Na/NZSP-0.15Ga/Na symmetric cells were assembled by affixing Na metal disks to each surface of NZSP-0.15Ga pellet to test the Na metal stripping/platting. Galvanostatic charge-discharge (GCD) for symmetric cells was carried out at 50 uA cm^{-2} on a LAND CT2001A/B instrument (Wuhan, China) at room temperature and each cycle was lasted for 1 h. And the direct current (DC) polarization measurement was performed on the Na/NZSP-0.15Ga/Ag cell to obtain the electronic conductivity. Na/NZSP-0.15Ga/stainless steel asymmetrical cells were assembled to examine the electrochemical stability window. Cyclic voltammetry (CV) was tested in the voltage range of -1 to 6V at a scanning rate of 0.5 mV s^{-1} using a BioLogic electrochemical station.

Solid-state Battery Fabrication and Measurements: 70 wt% active materials $Na_3V_2(PO_4)_3$ (Shenzhen Huaqing New Material Technology Co., Ltd), 20 wt% acetylene black and 10 wt% PVDF were mixed in N-methyl-2-pyrrolidone (NMP). The obtained homogeneous slurry was coated on the surface of the aluminum foil and dried at 120 ^{o}C in a vacuum oven overnight. Then the electrode was punched into 12 mm diameter to obtain $Na_3V_2(PO_4)_3$ (NVP) electrodes for electrochemical test. The mass loading of each NVP cathode was about 0.8-1.2 mg cm^{-2}. NVP cathode, NZSP-0.15Ga pellet and Na metal were assembled into 2032 coin cell in an Ar-filled glovebox. The liquid Na^{+} electrolyte (1 M $NaClO_4$ in EC:DMC:EMC, 1:1:1 by vol. with 5wt% FEC) was employed to improve the wettability of solid electrode-NVP cathode interface. All electrochemical tests were carried out on a LAND CT2001A/B (Wuhan, China) system. Electrochemical impedance spectroscopy (EIS) measurements were obtained on an SP-300 electrochemical station (BioLogic, France).

DFT calculation: The density functional theory (DFT) calculations have been conducted on Vienna ab-initio simulation package (VASP)[50,51] to study the doping process of Ga in $Na_3Zr_2Si_2PO_{12}$ crystal. The Projector augmented wave method[51] with a cutoff energy of 400 eV accompanied by Perdew-Burke-Ernzerhof functional[52] has been used in the DFT calculations. The (2×1×2) supercell of $Na_3Zr_2Si_2PO_{12}$ primitive cell has been used to build the doping model with one Zr-atom replaced by one Ga-atom and one Na-atom. All models have been fully relaxed with the energy convergence criterion of 10^{-5} eV and the force convergence criterion of 0.02 eV/Å, respectively. The reaction energy (E_r) has been calculated using following formula,

$$E_r=E_{doping}-E_{NZSP}-E_{Ga}+E_{Zr}-E_{Na}$$

The E_{doping}, E_{NZSP}, E_{Ga}, E_{Zr} and E_{Na} represent the energy of doping model, $Na_3Zr_2Si_2PO_{12}$ model, Ga-atom, Zr-atom and Na-atom, respectively.

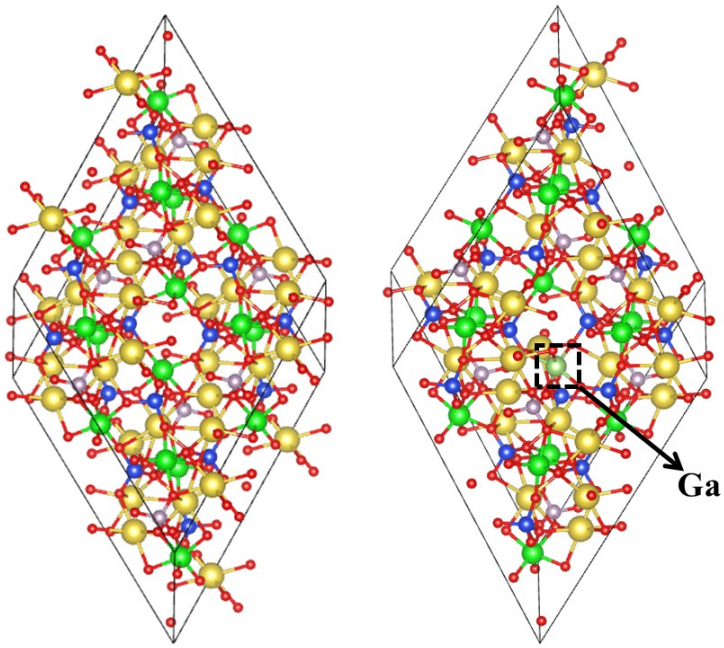

Figure S1. Structure of NASICON before and after introducing Ga.

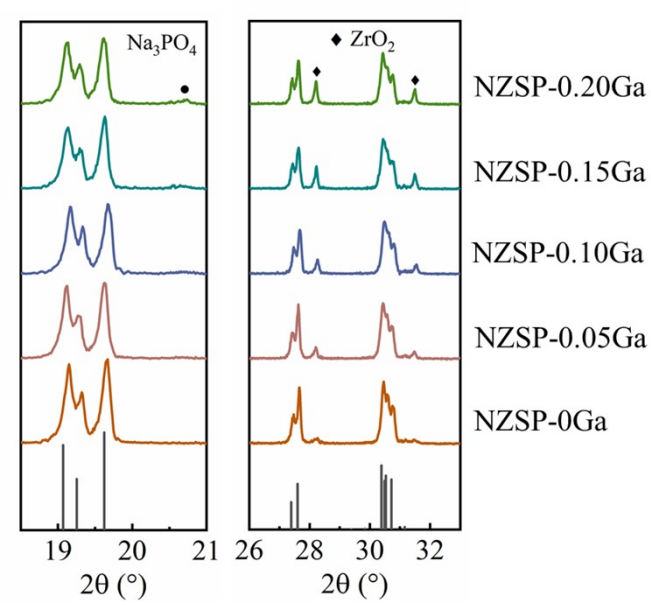

Figure S2. XRD patterns in the range between 18.5°-21° (c) and 29-35°.

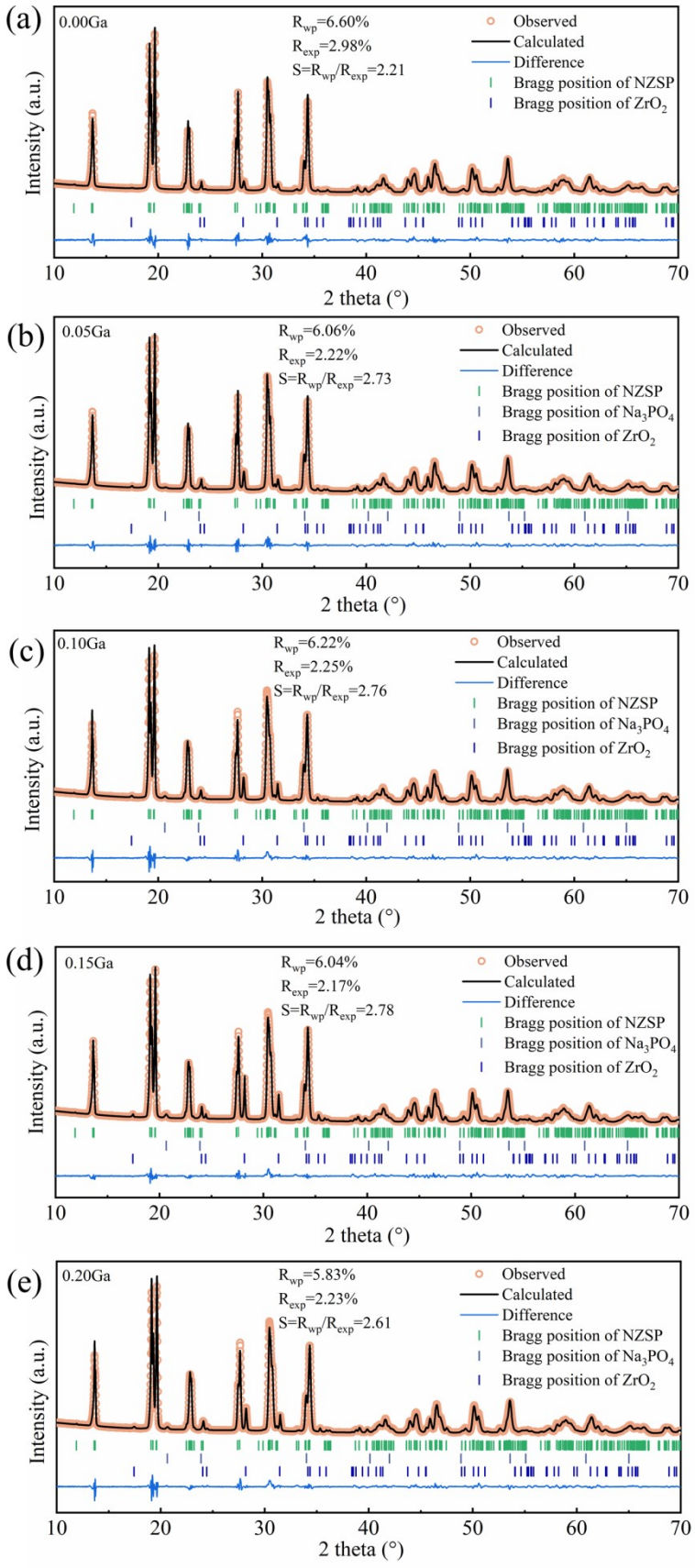

Figure S3. Rietveld refinement for NZSP-xGa (x=0, 0.05, 0.10, 0.15 and 0.20) based on powder XRD data.

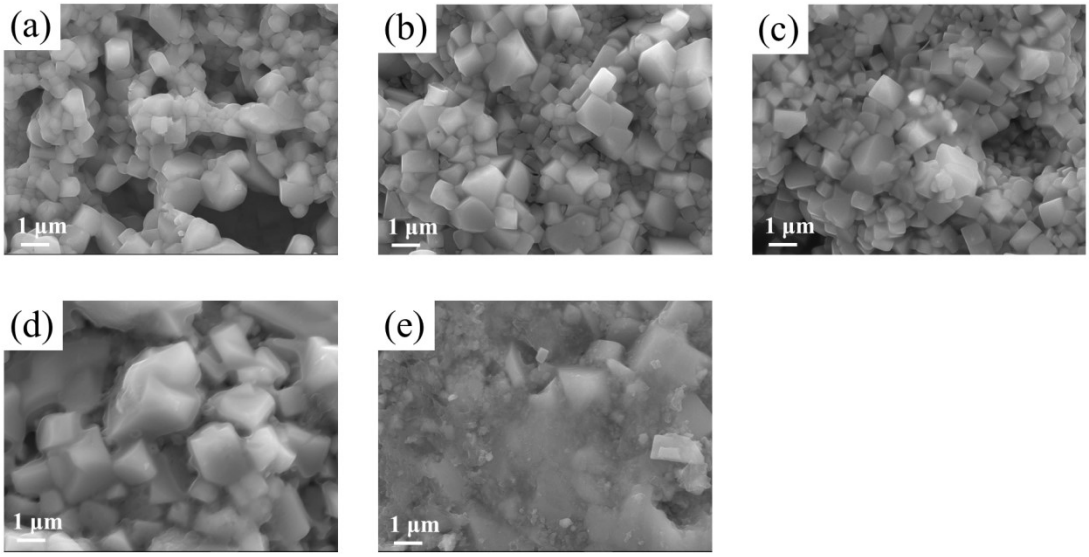

Figure S4. Cross-sectional SEM images of (a) NZSP-0Ga, (b) NZSP-0.05Ga, (c) NZSP-0.10Ga, (d) NZSP-0.15Ga and (e) NZSP-0.20Ga.

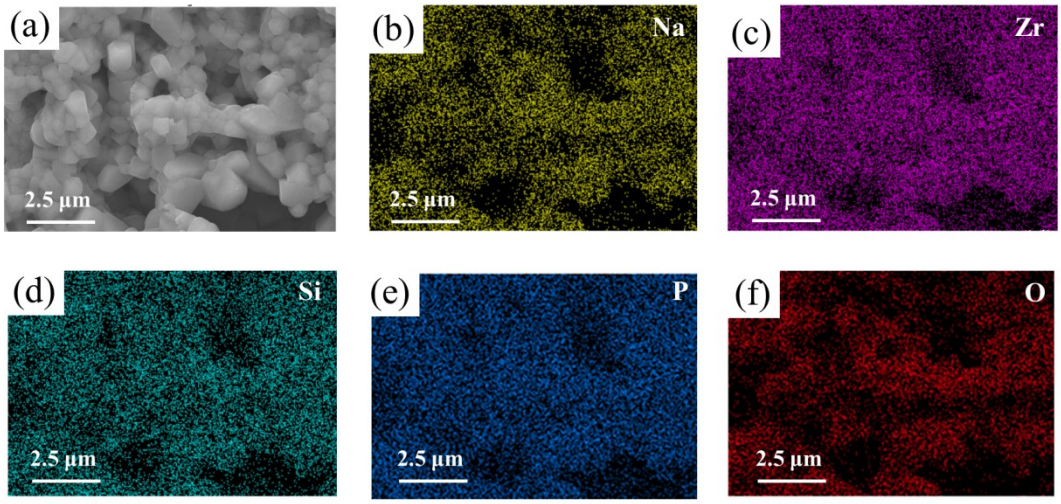

Figure S5. Elemental mapping of NZSP-0Ga.

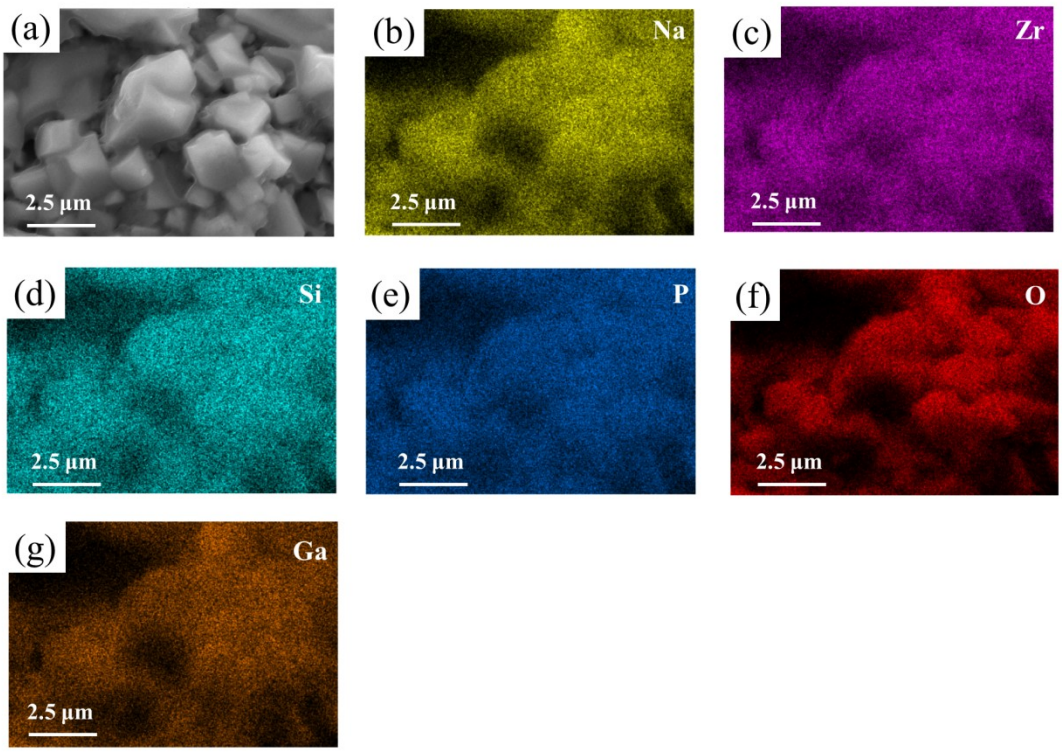

Figure S6. Elemental mapping of NZSP-0.15Ga.

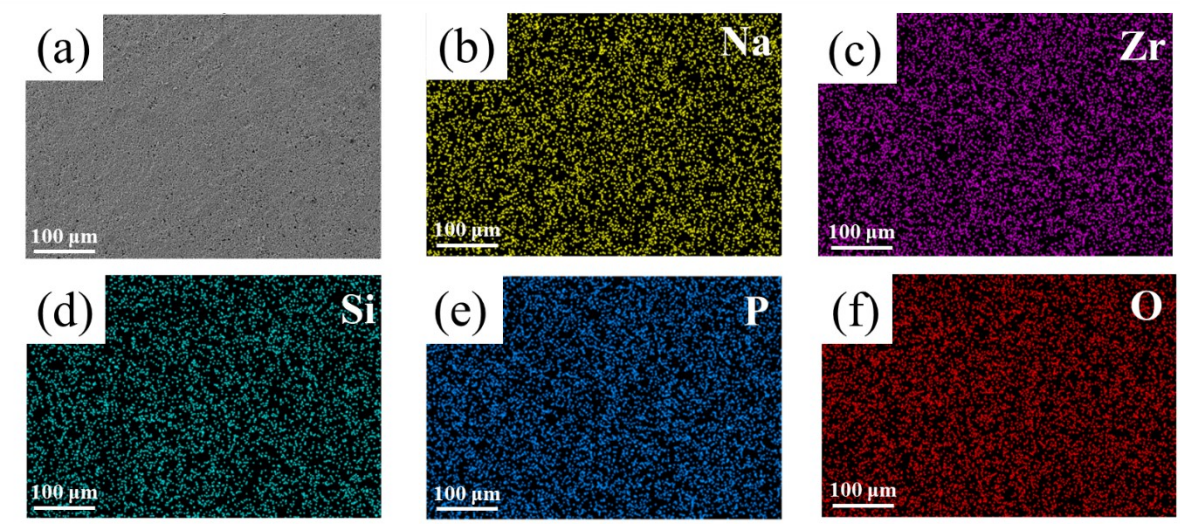

Figure S7. Elemental mapping with larger area of NZSP-0Ga.

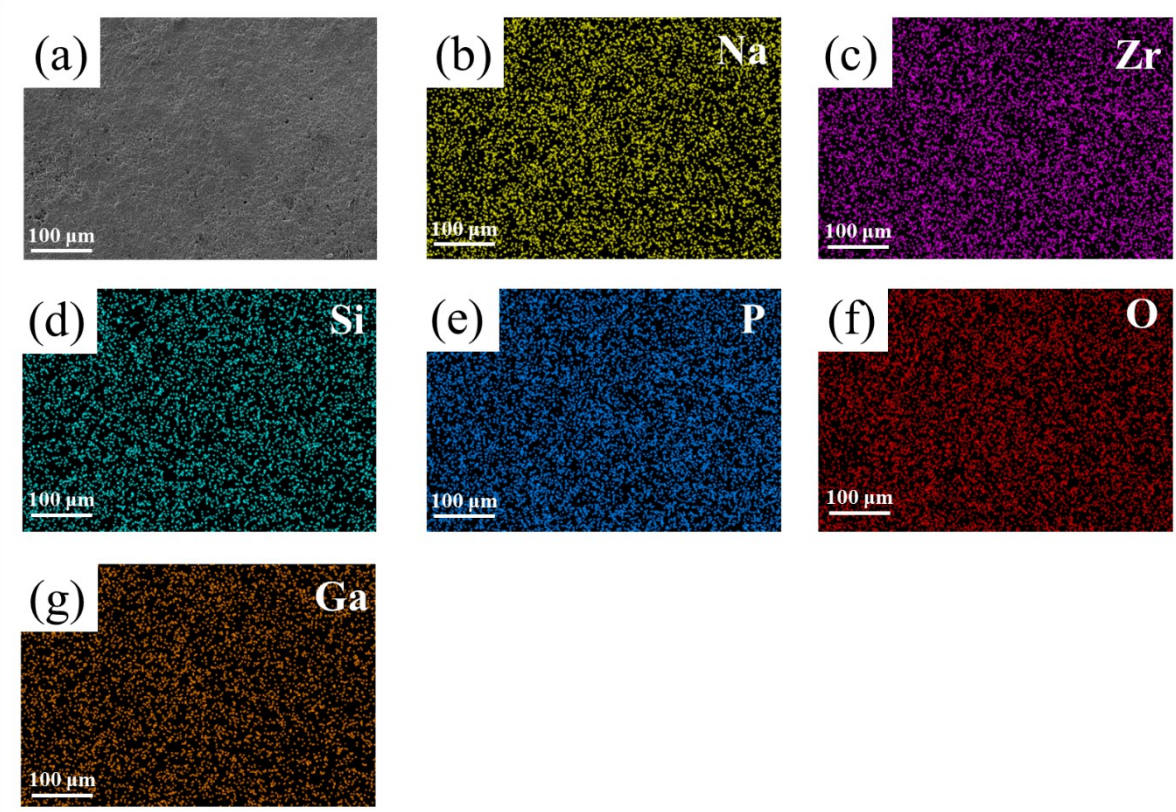

Figure S8. Elemental mapping with larger area of NZSP-0.15Ga.

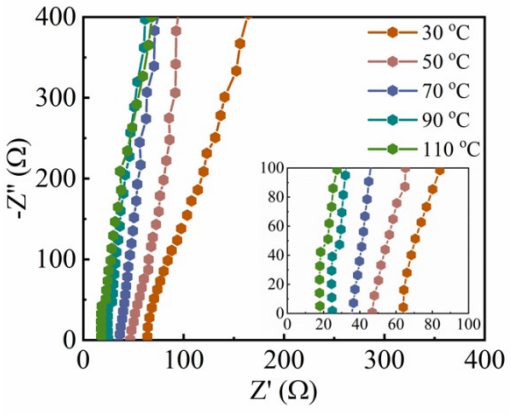

Figure S9. Nyquist plots of NZSP-0.15Ga at different temperatures.

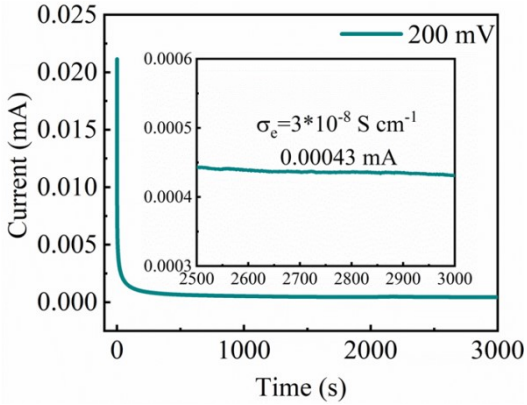

Figure S10. DC polarization curve for NZSP-0.15Ga under the applied voltage of 200 mV at room temperature.

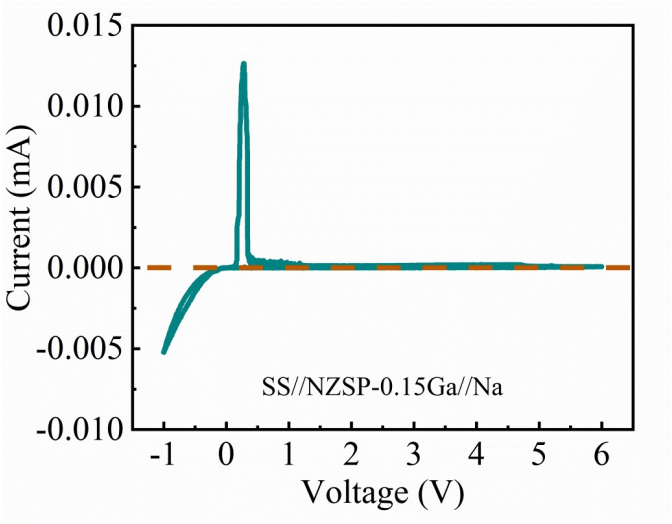

Figure S11. CV curve of SS/NZSP-0.15Ga/Na cell at a scanning speed of 5 mV s^{-1}.

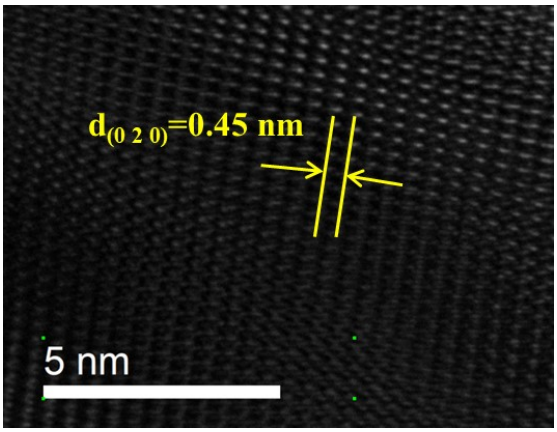

Figure S12. HRTEM of NZSP-0.15Ga.

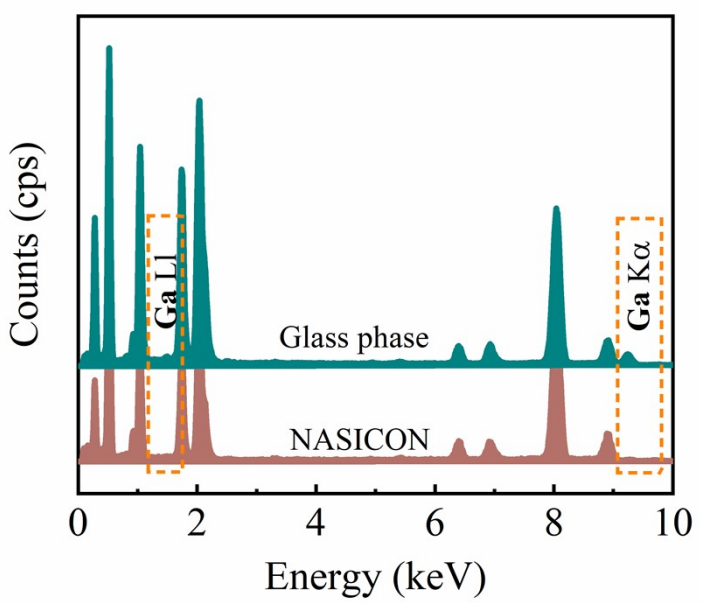

Figure S13. EDS point scanning of NZSP-0.15Ga.

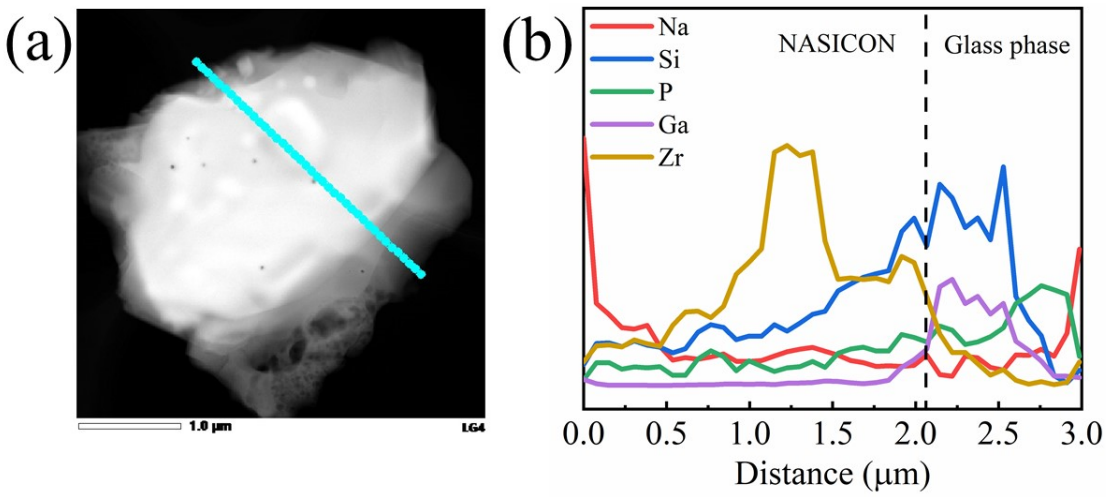

Figure S14. Dark-field STEM image of NZSP-0.15Ga and the EDS linear scanning. The sudden increase in Zr content is possibly due to the presence of ZrO_2.

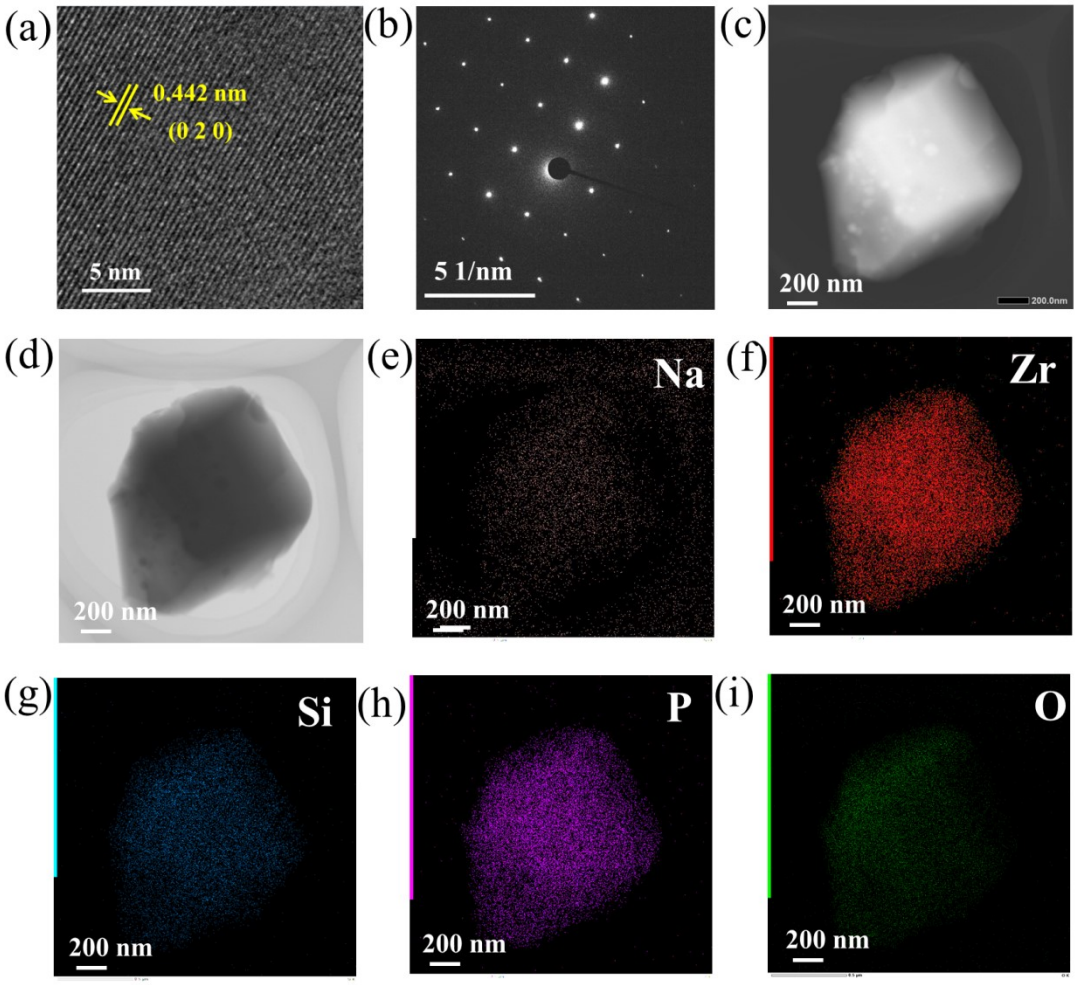

Figure S15. HRTEM, SAND and EDS mapping of NZSP-0Ga.

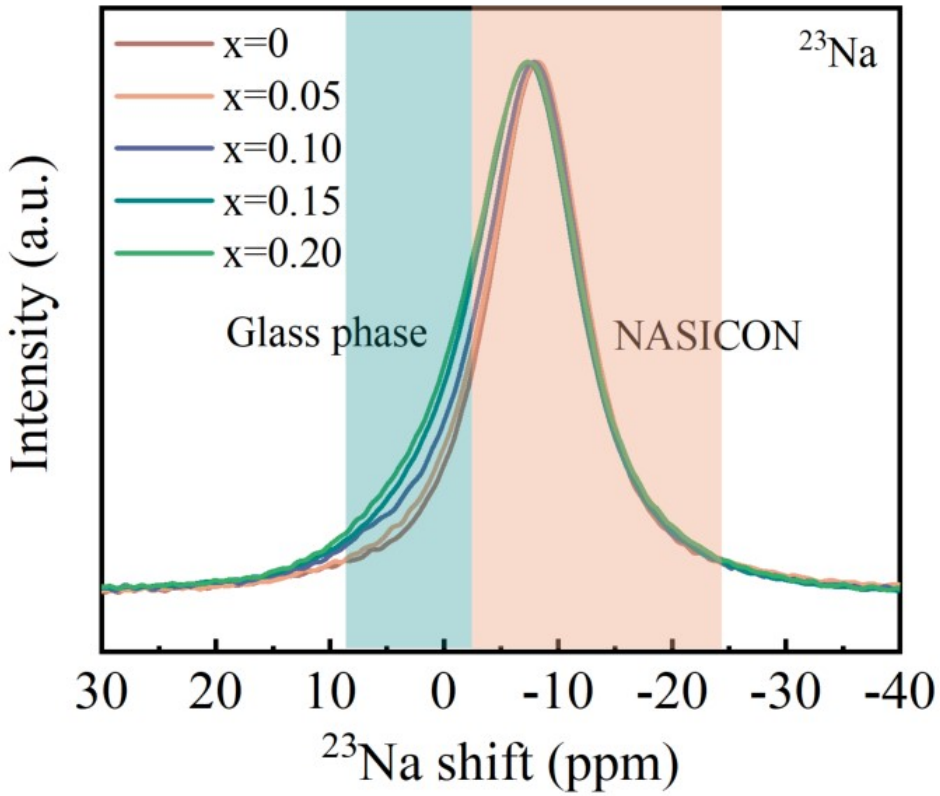

Figure S16. ^{23}Na spectra of NZSP-xGa acquired at 14.1 T.

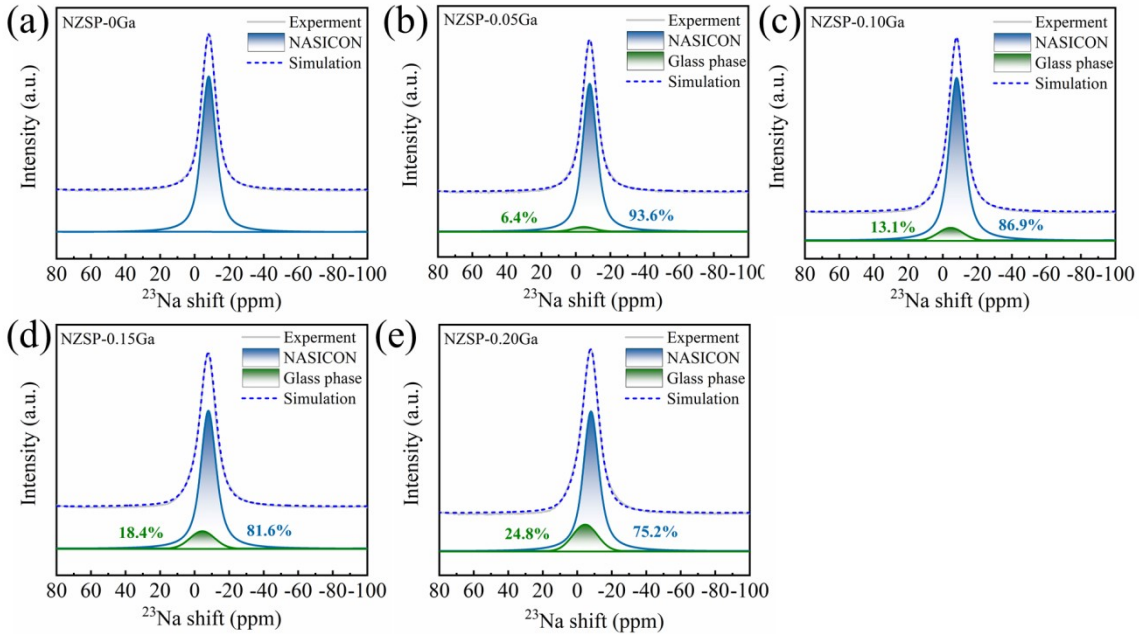

Figure S17. ^{23}Na spectra and deconvolution of NZSP-xGa acquired at 14.1 T.

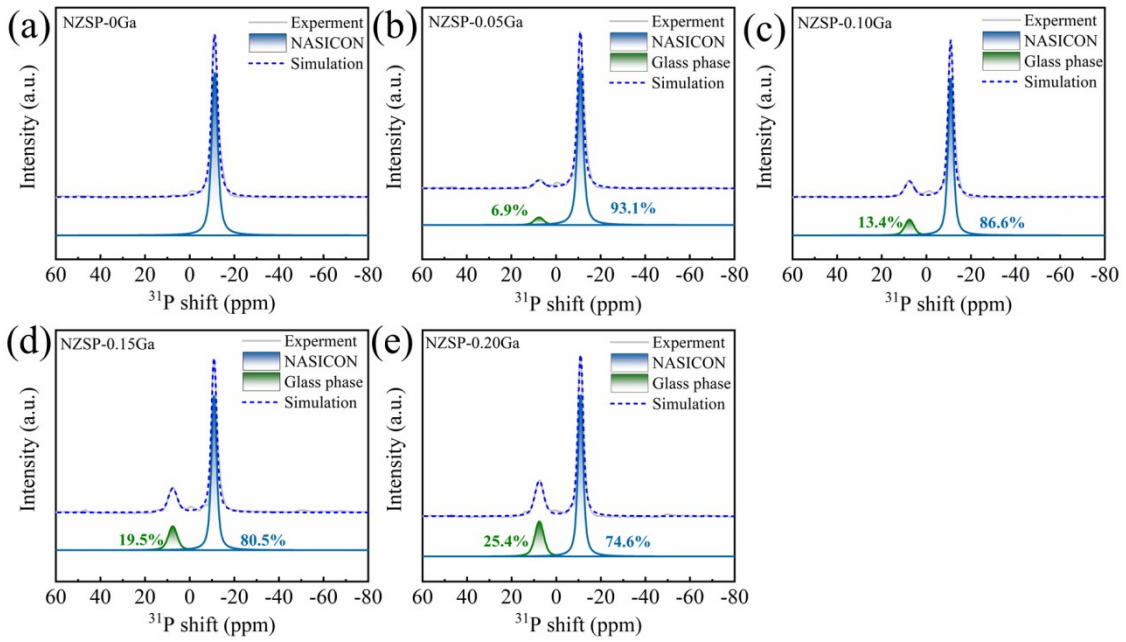

Figure S18. ^{31}P spectra and deconvolution of NZSP-xGa acquired at 14.1 T.

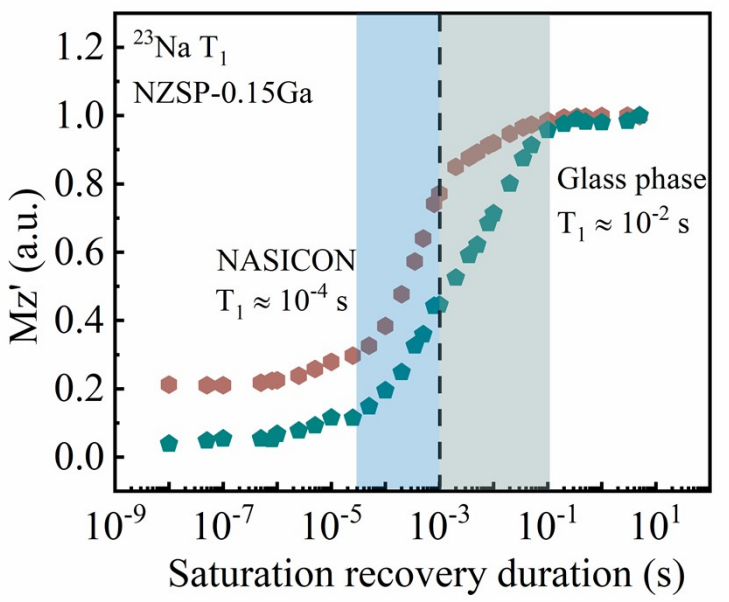

Figure S19. T_1 of NASICON and glass phase in NZSP-0.15Ga.

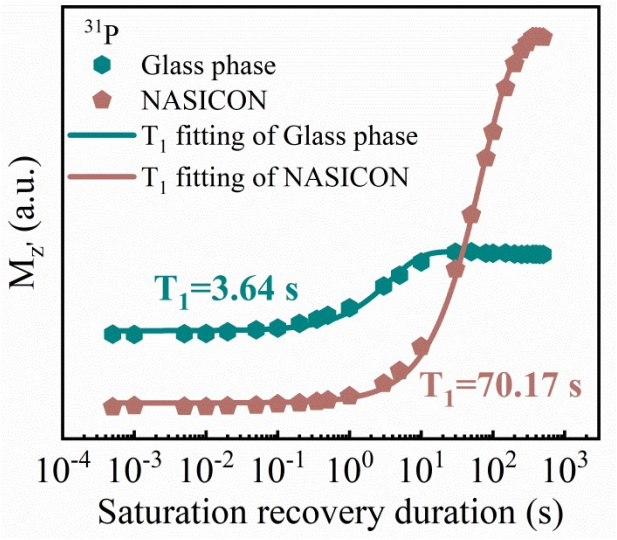

Figure S20. Saturation recovery fitting curves for ^{31}P relaxation.

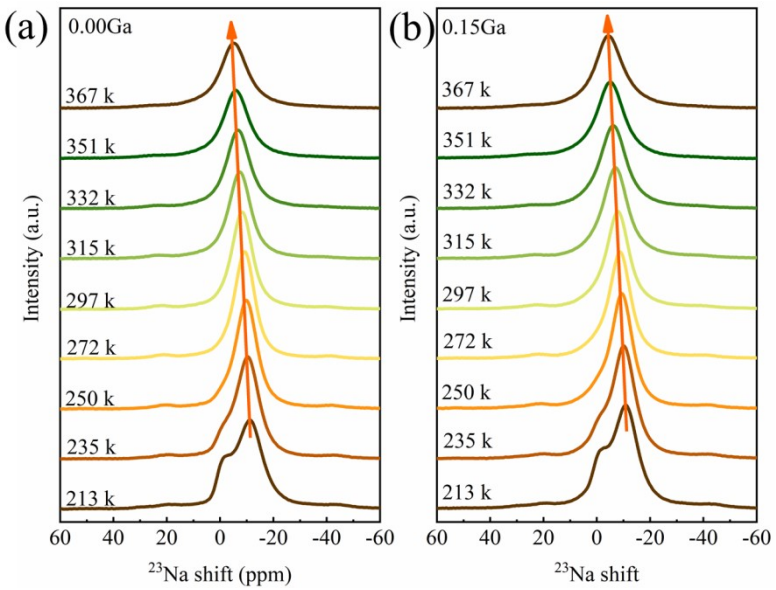

Figure S21. Solid-state ^{23}Na NMR spectra of NZSP-0Ga and NZSP-0.15Ga at different temperatures.

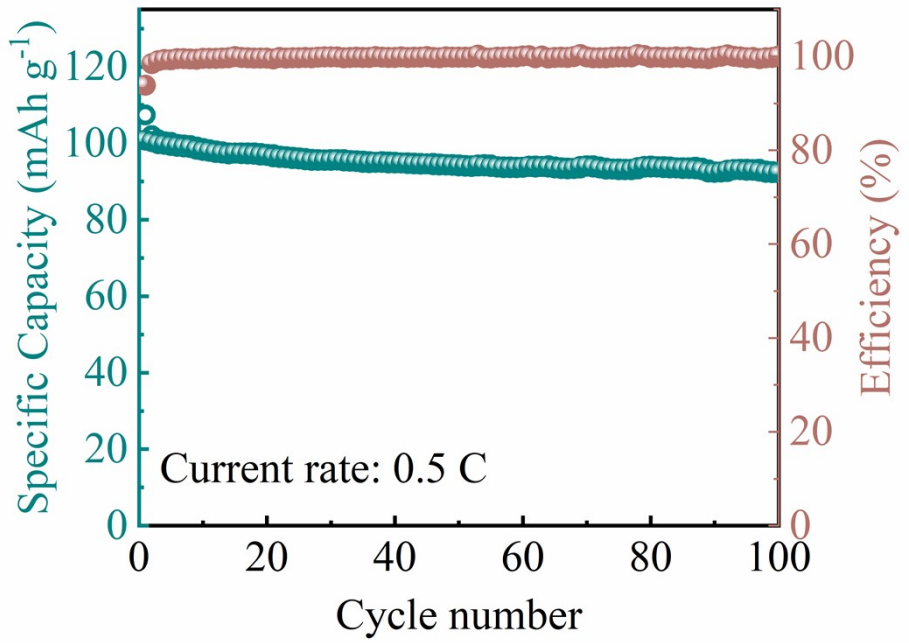

Figure S22. Cycling performance at 0.5 C.

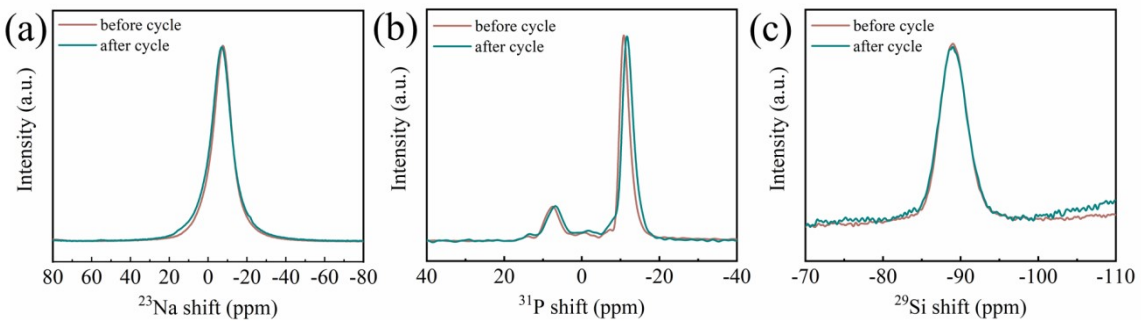

Figure S23. ^{23}Na, ^{31}P and ^{29}Si NMR spectra of NZSP-0.15Ga before and after cycling.

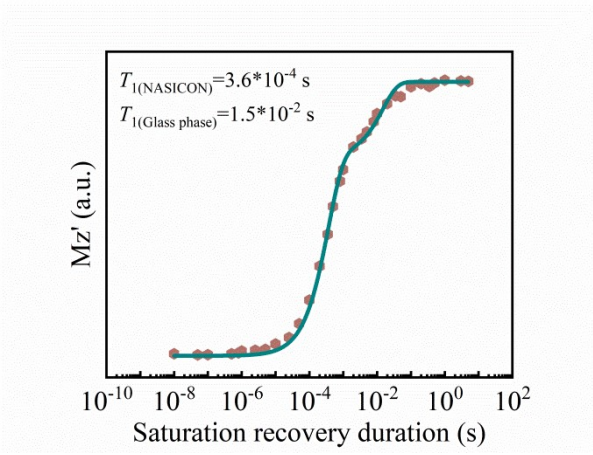

Figure S24. ^{23}Na saturation recovery fitting curve of the cycled NZSP-0.15Ga.

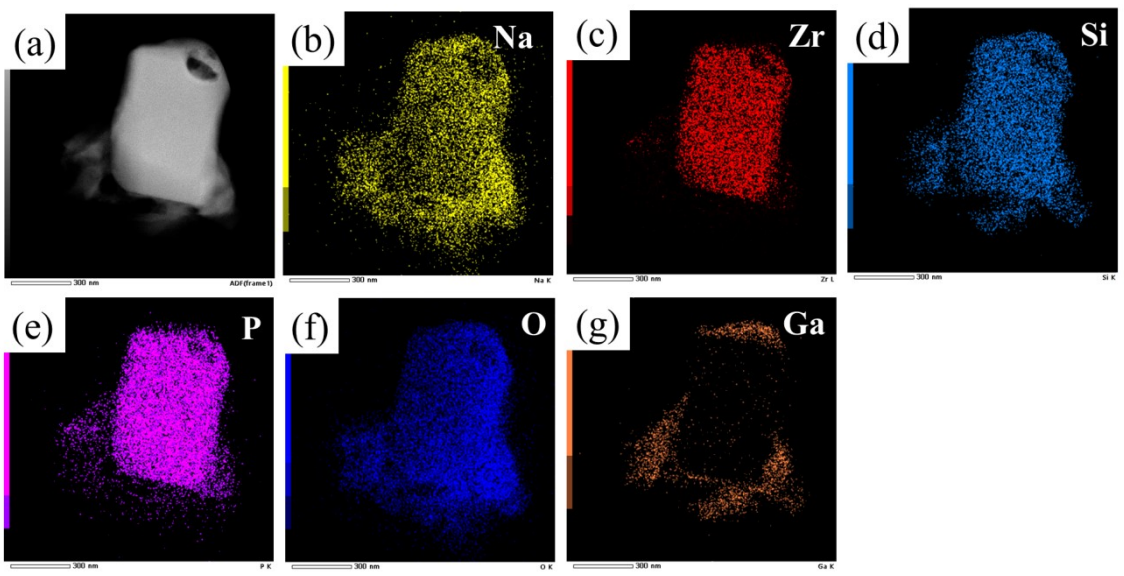

Figure S25. TEM and corresponding element-mapping images of NZSP-0.15Ga after 100 cycles.

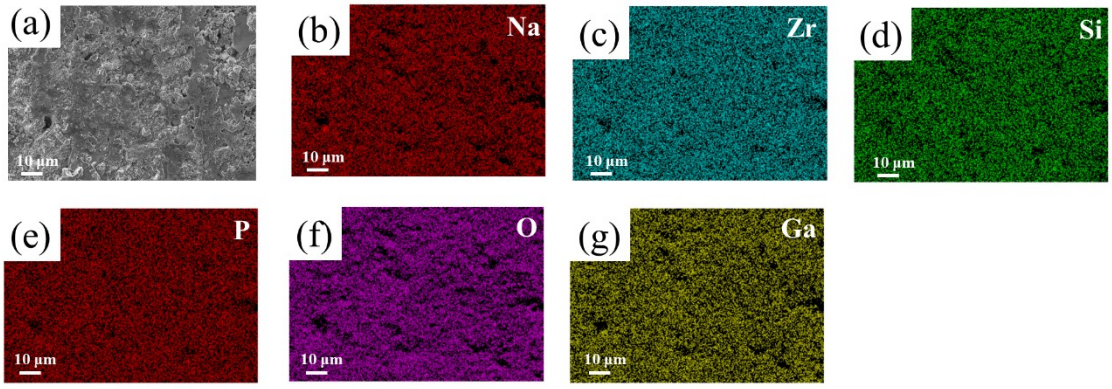

Figure S26. SEM and corresponding element-mapping images of NZSP-0.15Ga after 100 cycles.

Table S1. The calculated formation energies of NZSP, NZSP-Ga, Na, Ga and Zr from DFT.

Samples	Formation Energy(eV)
$Na_3Zr_2Si_2PO_{12}$	-1217.431
$Na_3Zr_2Si_2PO_{12}$-Ga	-1210.063
Na	-0.022
Ga	-0.035
Zr	-1.281

$E_{(reaction\ energy)}=E_{(doping)}-E_{(NZSP)}-E_{(Ga)}+E_{(Zr)}-E_{(Na)}$= -1210.063 - (-1217.431) - (-0.035) + (-1.281) - (0.022) = 6.144 eV

Table S2. Crystallographic data for the prepared NZSP-0.15Ga.

Crystal System			Monoclinic		
Space Group			C2/c		
Lattice Parameter			a = 15.670330, b = 9.065409 Å, c =		
Volume			9.216213 Å		
			V = 1086.997 Å^3		
Atoms	wyckoff positions	x	y	z	Occupancy
Na1	4d	0.25000	0.25000	0.50000	0.81000
Na2	4e	0.50000	0.90000	0.25000	1.00000
Na3	8f	0.82925	0.07614	0.84174	0.60000
Zr1	8f	0.10092	0.24738	0.05477	1.00404
Ga1	8f	0.10092	0.24738	0.05477	-0.00404
Si1	4e	0.00000	0.02951	0.25000	0.67000
Si2	8f	0.34724	0.09152	0.24800	0.67000
P1	4e	0.00000	1.03127	0.25000	0.33000
P2	8f	0.36440	0.13262	0.27428	0.33000
O1	8f	0.15194	0.43329	0.22642	1.00000
O2	8f	0.43228	0.44810	0.08322	1.00000
O3	8f	0.25995	0.17807	0.21762	1.00000
O4	8f	0.38203	0.13336	0.11787	1.00000
O5	8f	0.45195	0.17250	0.45009	1.00000
O6	8f	0.08796	0.12916	0.24874	1.00000

Table S3. Crystallographic data for the prepared NZSP-0Ga.

Crystal System			Monoclinic		
Space Group			C2/c		
Lattice Parameter			a = 15.664660, b = 9.058880 Å, c =		
Volume			9.217207 Å		
			V = 1086.298 Å^3		
Atoms	wyckoff positions	x	y	z	Occupancy
Na1	4d	0.25000	0.25000	0.50000	0.81000
Na2	4e	0.50000	0.89710	0.25000	1.00000
Na3	8f	0.83151	0.08192	0.83788	0.60000
Zr1	8f	0.10133	0.24925	0.05587	1.00000
Si1	4e	0.00000	0.02599	0.25000	0.67000
Si2	8f	0.34807	0.09685	0.24922	0.67000
P1	4e	0.00000	0.05499	0.25000	0.33000
P2	8f	0.37693	0.14245	0.29205	0.33000
O1	8f	0.15745	0.44017	0.22477	1.00000
O2	8f	0.42917	0.45051	0.07746	1.00000
O3	8f	0.25771	0.17599	0.20972	1.00000
O4	8f	0.38298	0.13555	0.11628	1.00000
O5	8f	0.45599	0.17413	0.45740	1.00000
O6	8f	0.08627	0.13964	0.23914	1.00000

Table S4. Crystallographic data for the prepared NZSP-0.05Ga.

Crystal System			Monoclinic		
Space Group			C2/c		
Lattice Parameter			a = 15.661112, b = 9.058272 Å, c =		
Volume			9.219478 Å		
			V = 1086.388 $Å^3$		
Atoms	wyckoff positions	x	y	z	Occupancy
Na1	4d	0.25000	0.25	0.5	0.81
Na2	4e	0.50000	0.89693	0.25000	1.00000
Na3	8f	0.82833	0.07734	0.83951	0.60000
Zr1	8f	0.10138	0.24860	0.05568	0.99409
Ga1	8f	0.10138	0.24860	0.05568	0.00591
Si1	4e	0.0000	0.02803	0.25000	1.03626
Si2	8f	0.35227	0.10550	0.25444	0.96739
P1	4e	0.00000	1.07576	0.25000	0.09890
P2	8f	0.38811	0.19263	0.33870	0.13521
O1	8f	0.15300	0.44035	0.23071	1.00000
O2	8f	0.43001	0.44873	0.07929	1.00000
O3	8f	0.25721	0.17857	0.21130	1.00000
O4	8f	0.38145	0.13664	0.11916	1.00000
O5	8f	0.45406	0.17598	0.45500	1.00000
O6	8f	0.08655	0.13174	0.24446	1.00000

Table S5. Crystallographic data for the prepared NZSP-0.10Ga.

Crystal System			Monoclinic		
Space Group			C2/c		
Lattice Parameter			a = 15.670330, b = 9.065409 Å, c =		
Volume			9.216213 Å		
			V = 1086.997 Å^3		
Atoms	wyckoff positions	x	y	z	Occupancy
Na1	4d	0.25000	0.25000	0.50000	0.81000
Na2	4e	0.50000	0.89981	0.25000	1.00000
Na3	8f	0.82732	0.08268	0.84023	0.60000
Zr1	8f	0.10125	0.24809	0.05528	0.99930
Ga1	8f	0.10125	0.24809	0.05528	0.00070
Si1	4e	0.00000	0.02886	0.25000	0.67000
Si2	8f	0.34627	0.09440	0.24828	0.67000
P1	4e	0.00000	1.04819	0.25000	0.33000
P2	8f	0.36972	0.13584	0.27819	0.33000
O1	8f	0.15311	0.43892	0.22673	1.00000
O2	8f	0.43056	0.44862	0.08146	1.00000
O3	8f	0.25876	0.17865	0.21496	1.00000
O4	8f	0.38202	0.13352	0.12061	1.00000
O5	8f	0.45080	0.17425	0.45036	1.00000
O6	8f	0.08663	0.13094	0.24490	1.00000

Table S6. Crystallographic data for the prepared NZSP-0.20Ga.

Crystal System		Monoclinic			
Space Group		C2/c			
Lattice Parameter		a = 15.670330, b = 9.065409 Å, c =			
Volume		9.216213 Å			
		V = 1086.997 Å^3			
Atoms	wyckoff positions	x	y	z	Occupancy
Na1	4d	0.25000	0.25000	0.50000	0.81000
Na2	4e	0.50000	0.89923	0.25000	1.00000
Na3	8f	0.83134	0.07555	0.84094	0.60000
Zr1	8f	0.10071	0.24708	0.05447	0.92149
Ga1	8f	0.10071	0.24708	0.05447	0.07851
Si1	4e	0.00000	0.03684	0.25000	0.67000
Si2	8f	0.34600	0.09234	0.24695	0.67000
P1	4e	0.00000	1.02766	0.25000	0.33000
P2	8f	0.36730	0.13017	0.27251	0.33000
O1	8f	0.15415	0.43275	0.22797	1.00000
O2	8f	0.42995	0.44732	0.08129	1.00000
O3	8f	0.26014	0.17987	0.22029	1.00000
O4	8f	0.38167	0.13167	0.11631	1.00000
O5	8f	0.45315	0.17324	0.45223	1.00000
O6	8f	0.08795	0.12740	0.24914	1.00000

Table S7. Activation energy of NZSP-xGa samples from AC impedance analysis.

Samples	Activation energy (eV)
x=0.05	0.22
x=0.10	0.18
x=0.15	0.16
x=0.20	0.17

Table S8. Simulations results from ^{23}Na NMR data.

Samples	Phase	Shift (ppm)	C_Q	η	Population
x=0.00	NASICON	-3.3	2	0.8	100%
x=0.05	NASICON	-3.4	2	0.8	
	Glass phase	-0.2	1.9	0.8	6.4%
x=0.10	NASICON	-3.4	2	0.8	
	Glass phase	-0.2	1.9	0.8	13.1%
x=0.15	NASICON	-3.5	2	0.8	
	Glass phase	-0.2	1.9	0.8	18.4%
x=0.20	NASICON	-3.5	2	0.8	
	Glass phase	-0.2	1.9	0.8	24.8%

Table S9. Simulations results from ^{31}P NMR data.

Samples	Phase	Shift (ppm)	Population
x=0.00	NASICON	-11.2	100%
x=0.05	NASICON	-11.0	
	Glass phase	7.6	6.9%
x=0.10	NASICON	-11.0	
	Glass phase	7.6	13.4%
x=0.15	NASICON	-11.0	
	Glass phase	7.6	19.5%
x=0.20	NASICON	-11.0	
	Glass phase	7.6	25.4%

Table S10. A survey of electrochemical performances of $Na_3Zr_2Si_2PO_{12}$-based symmetric batteries.

Electrolytes	**Operating temperature**	**Current densities** (mA cm^{-2})	**Cycle time**	**Ref.**
$Na_3Zr_2Si_2PO_{12}$-0.15Ga	**RT**	**0.2**	**800 h**	**This work**
		0.4	**200 h**	
$Na_{3.125}Zr_{1.75}Sc_{0.125}Ge_{0.125}Si_2PO_{12}$	RT	0.2	500 h	Energy Storage Materials 40 (2021) 282–291
$Na_3Zr_2Si_2PO_{12}$	RT	0.1	800 h	ACS Appl. Energy Mater. 2020, 3, 7427−7437
SnO_x/Sn-$Na_3Zr_2Si_2PO_{12}$	RT	0.1	1500 h	Small Methods 2021, 2100339
		0.3	500 h	
$Na_3Zr_2Si_2PO_{12}$-0.10MgF_2	27 °C	0.5	100 h	ChemElectroChem, 2020, 7(9): 2087-2094.
$Na_3Zr_2Si_2PO_{12}$-with 450 °C heat treatment	RT	0.3	250 h	Chem. Mater. 2020, 32, 3970−3979
$Na_{3.4}Zr_{1.6}Sc_{0.4}Si_2PO_{12}$	25 °C	0.1	800 h	Cell Reports Physical Science 2, 100478, July 21, 2021
		0.2	700 h	
$Na_3Zr_2Si_2PO_{12}$	25 °C	0.1	2000 h	Small **2021**, 2100974
	25 °C	0.2	1000 h	
$Na_{3.2}Zr_{1.9}Ca_{0.1}Si_2PO_{12}$	25 °C	0.3	400 h	Adv. Energy Mater. 2019, 1901205