Supplementary Information

Vacancy-controlled quaternary sulfide $Na_{3-x}Zn_{1-x}Ga_{1+x}S_4$ with improved ionic conductivity and aqueous stability

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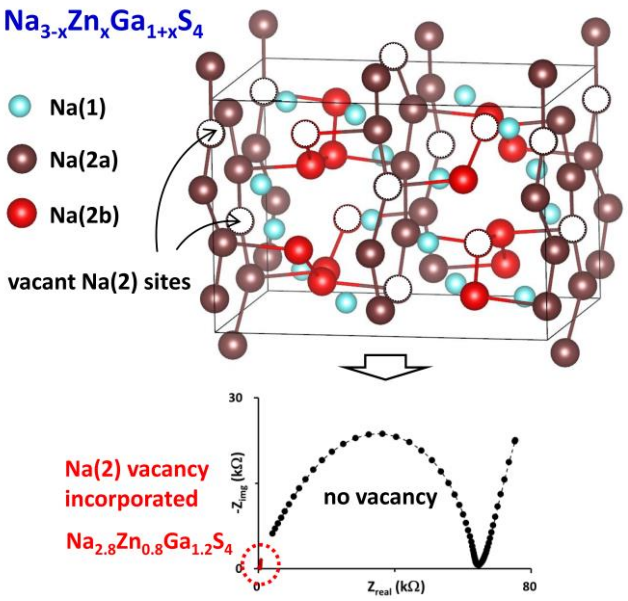

Contents

Experimental details

Synthesis and characterizations: Unless otherwise mentioned, all chemicals with purity greater than 99% were purchased from Merck and used without further purification. Na_2S and Ga_2S_3 were obtained from Alfa Aesar. CF (MTI Corp.) was used for electron conducting in the study on the redox behaviors of SSEs and TiS_2.

For the synthesis of $Na_{3-x}Zn_{1-x}Ga_{1+x}S_4$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, and 0.50) and $Na_{3-x}Zn_{1-x}Ga_{1+x}Se_4$ (x = 0, 0.10, 0.20), appropriate amounts of Na_2S, Zn, Ga_2S_3 (or Ga_2Se_3), and S (or Se) were ball-milled in an Ar-filled glove box for 10 min and the mixture was transferred to a quartz tube. After flame-sealing under vacuum (NBD-DXZ-02, Nobody Sci. Tech. Co., China), the tube was placed in a box furnace and heated to 750°C (heating rate = 5°C min^{-1}, duration = 12 h). The tube was slowly cooled to 400°C (-5°C h^{-1}) and naturally cooled to RT. For comparison, Na_3PS_4 and Na_3SbS_4 were also synthesized via the similar procedure. The mixture of Na_2S, P_2S_5, and S for Na_3PS_4 was heat-treated in a sealed quartz tube at 270°C. Na_3SbS_4 was synthesized from Na_2S and Sb_2S_3 at 550°C. Na_2Sn alloy was prepared via ball-milling elemental Na scraps and Sn powder for 2 h.

XRD patterns were collected for the samples in an air-tight holder, using a Rigaku ULTIMA 4 diffractometer with a Cu K_α radiation source at a scan rate of 2.5° min^{-1}. Rietveld refinement of the XRD data was performed using a Fullprof package. To define the background and the peak shape, a linear interpolation and a pseudo-Voigt function were selected, respectively. The nominal compositions were used for the refinement and the relative SOF between Na(1) and Na(2) was allowed to vary. BVEL studies were also performed with the BondStr program embedded in the Fullprof package.

Cell fabrication and electrochemical tests: For EIS measurements and DC polarization tests, SS|SSE|SS cells were fabricated. SSE powders (200 mg) were hand-ground and sandwiched between SS discs. The powder was pelletized within a POM (polyoxymethylene) mold under a pressure of 300 MPa (Specac Ltd). Typically, a pellet has a thickness of ca. 500 μm and an area of 1.33 cm^2. Hot-pressed pellet was made using a PEEK (polyether ether ketone) mold on

a hot press (200°C, 10 min, YLJ-HP60-LD, MTI Corp.). For ESW studies using a Na|SSE|SSE+CF|SS cell, the mixture of SSE and CF was made by ball-milling 50mg each. A cathode composite in a $Na_2Sn|Na_{2.8}Zn_{0.8}Ga_{1.2}S_4|TiS_2$ full cell was prepared by mixing $Na_{2.8}Zn_{0.8}Ga_{1.2}S_4$ (50%), TiS_2 (45%) and CF (5%) in N-methyl-2-pyrrolidone and by vacuum-drying at 150°C. The total mass of a composite was ca. 3 mg.

The EIS spectra were recorded by applying a sine wave of ±10.0 mV within a frequency range from 2 MHz to 0.1 Hz (SP2, WonATech). An automatic WBCS 3000 battery cycler (WonATech) was used for voltametric and galvanostatic studies.

Simulations: For DFT calculations, we used the Vienna ab initio Simulation Package (VASP6.1),[1-3] based on the projector augmented-wave approach with the Perdew−Burke−Ernzerhof generalized-gradient approximation.[4] A cutoff energy of 520 eV and a k-point grid of at least 1000/(number of atoms in the cell) was used for all calculations. The structural relaxation was implemented with the convergence thresholds for the total energy and ionic force components of 10^{-5} eV and 0.02 eV/Å.

The voltage stability window of a compound was calculated referring to the phase diagram constructed using pymatgen software package.[5] Recently discovered $NaGaS_2$ and Na_5GaS_4 structures, which are missing in materials project (MP) library,[6,7] were taken after literatures.[8,9] The Rietveld refinement was conducted for $Na_{3-x}Zn_{1-x}Ga_{1+x}S_4$ to define the model structure for DFT calculations, and a huge amount of configurations for x = 0, 0.1, 0.2 were taken into account, such that 10 lowest-Coulomb-energy entries were selected using a supercell program,[10,11] among which the lowest configuration was chosen as a model structure for AIMD calculations. In analogy, the formation energy calculation for $Na_{3-x}Zn_{1-x}Ga_{1+x}S_4$ (1 vac, 2 vac, and 3 vac, corresponding to x = 0.06, 0.12, and 0.19) led to a configuration issue induced by the vacancy in the Na(1) site and Na(2) site. We also selected 10 lowest-Coulomb-energy entries using the supercell program.

To examine the ion conductivities and activation energies of the selected candidates, AIMD calculations were implemented at 600, 800, 1000, and 1200K.[12,13] A cutoff energy was

set as 280 eV and non-spin-polarized calculations were performed using a single Γ-center k-point grid for all calculations. The MSD for 50 ps with a time step of 2 fs was obtained through the AIMD based on the canonical ensemble (NVT) and Nosé–Hoover thermostat algorithm. For more reliable diffusivity calculations, we repeated the MSD calculation procedures twice. The calculation protocol proposed by Fang and Jena, and He et al.[14,15] was followed. Pymatgen-diffusion packages was partly altered and used for the diffusivity calculation.[5]

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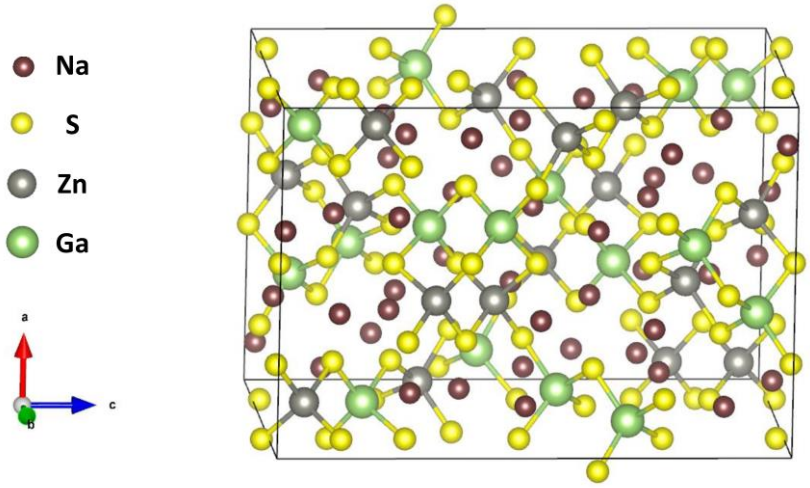

Figure S1. The most stable Zn/Ga distribution, determined via Coulomb energy and DFT formation energy calculations. The fractional coordinates of Zn: (0.07860, 0.12750, 0.81190), (0.42140, 0.87250, 0.31190), (0.37750, 0.17140, 0.56190), (0.12250, 0.82860, 0.06190), (0.87750, 0.82860, 0.56190), (0.62250, 0.17140, 0.06190), (0.92140, 0.87250, 0.18810), (0.57860, 0.12750, 0.68810), (0.92140, 0.62750, 0.68810), (0.57860, 0.37250, 0.18810), (0.62250, 0.67140, 0.93810), (0.87750, 0.32860, 0.43810), (0.07860, 0.37250, 0.31190), (0.42140, 0.62750, 0.81190), (0.12250, 0.32860, 0.93810), (0.37750, 0.67140, 0.43810).

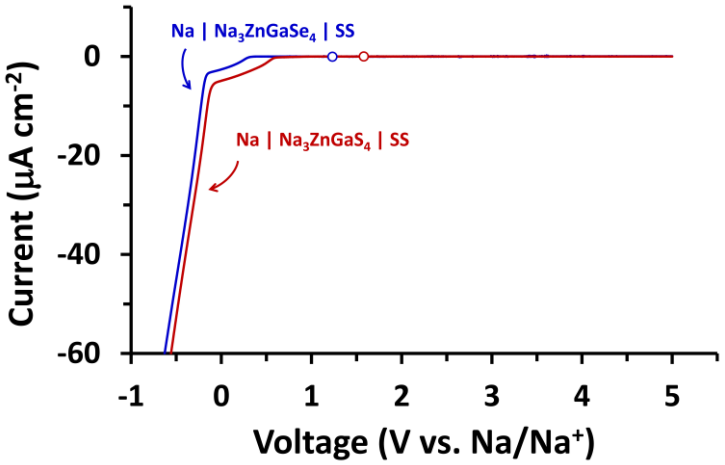

Figure S2. LSV at a scan rate of 0.1 mV s^{-1}. Open circles indicate open-circuit voltages, from which the voltage was scanned in either negative or positive directions.

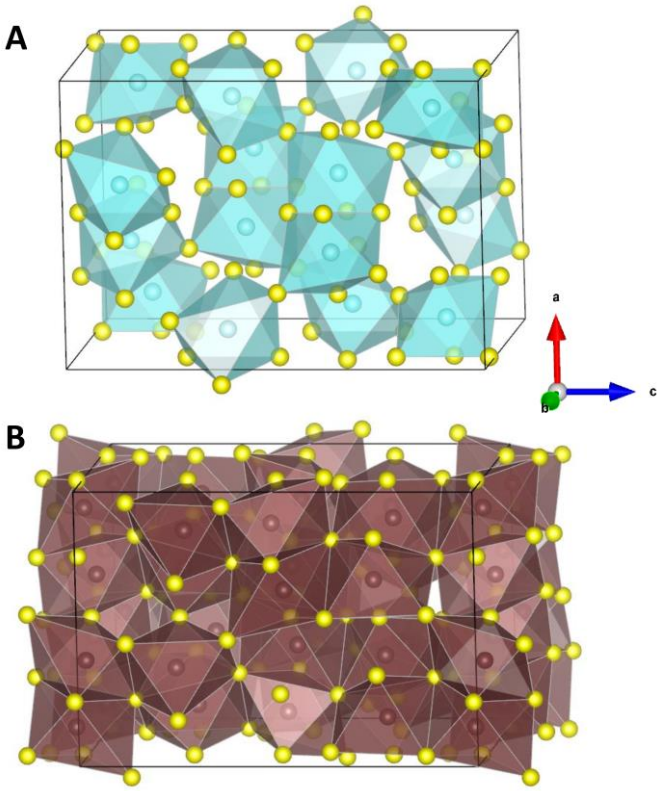

Figure S3. Polyhedron connectivity (A) $Na(1)S_6$ and (B) $Na(2)S_6$. Due to corner-shared nature between Na(1) octahedra in (A), Na(1)-Na(1) conduction is expected to be low.

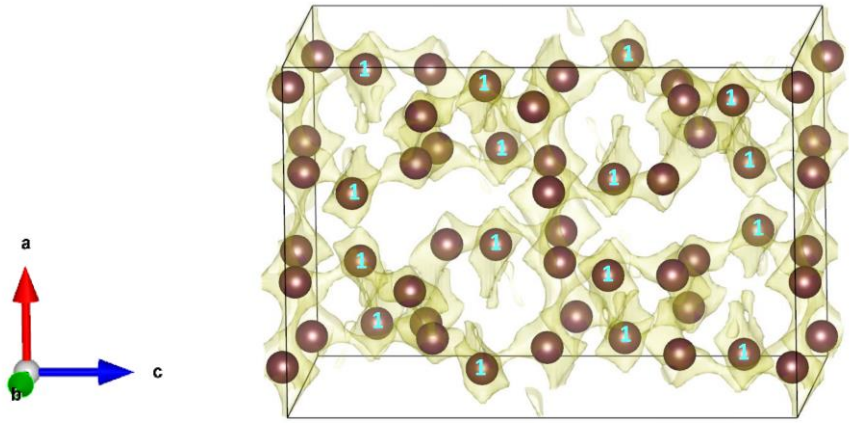

Figure S4. Iso-energy surfaces of -1.1 eV with E_{min} = -1.81 eV. Percolation threshold was +0.66 eV (E = -1.15 eV) along a-axis and b-axis, and +0.58 eV (E = -1.23 eV) to c-axis direction. It is obvious that Na(1) sites have no conduction channels. Only isolated contours are evident.

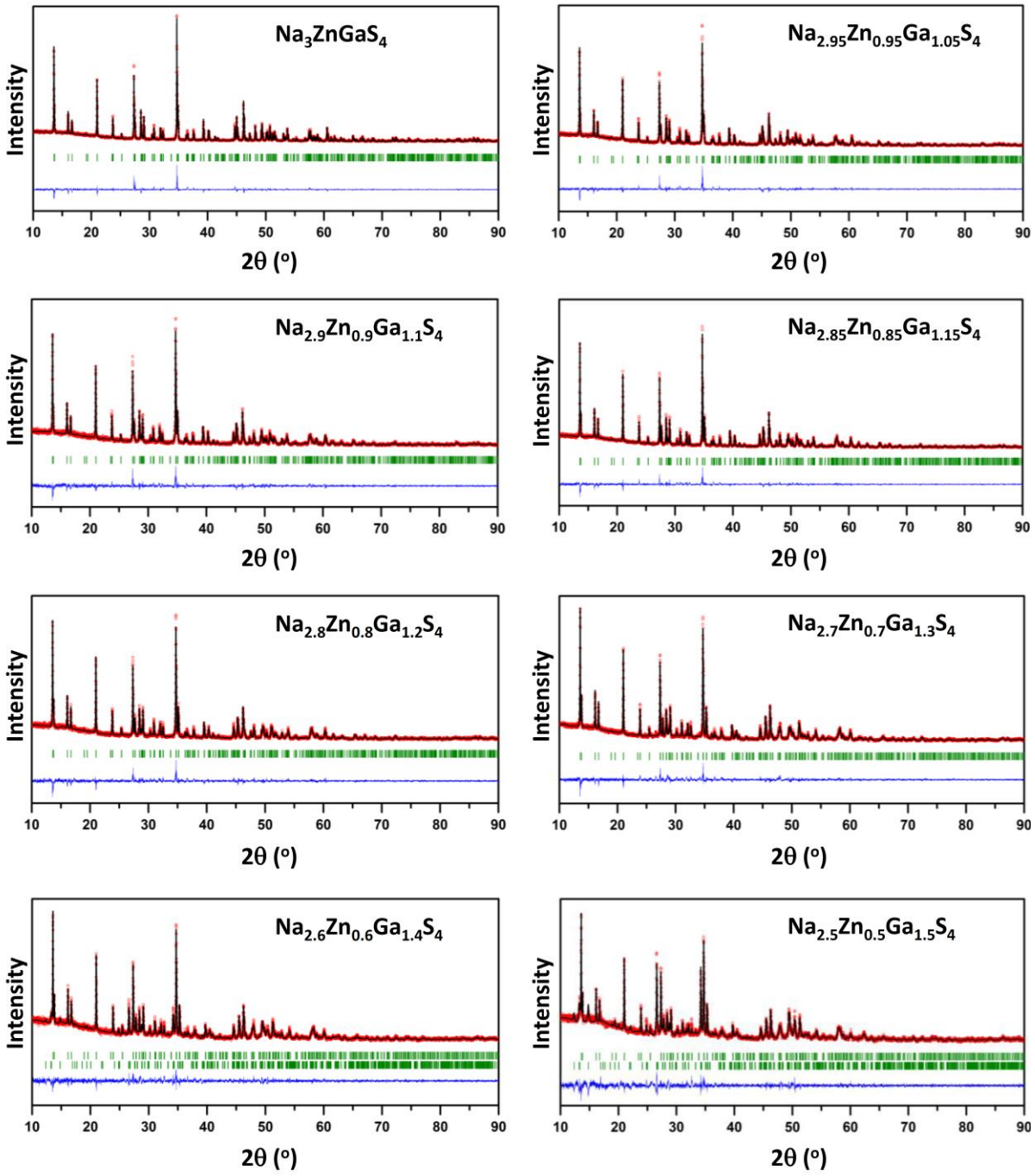

Figure S5. Full-pattern Rietveld refinement of XRD patterns for $Na_{3-x}Zn_{1-x}Ga_{1+x}S_4$ using the $I4_1/acd$ structure. Red dots, black line, and blue line represent the experimental, calculated, and difference profiles, respectively. The green vertical tick marks denote the position of Bragg reflections. For x = 0.4 and 0.5, the $NaGaS_2$ impurity phase was included in the refinement.

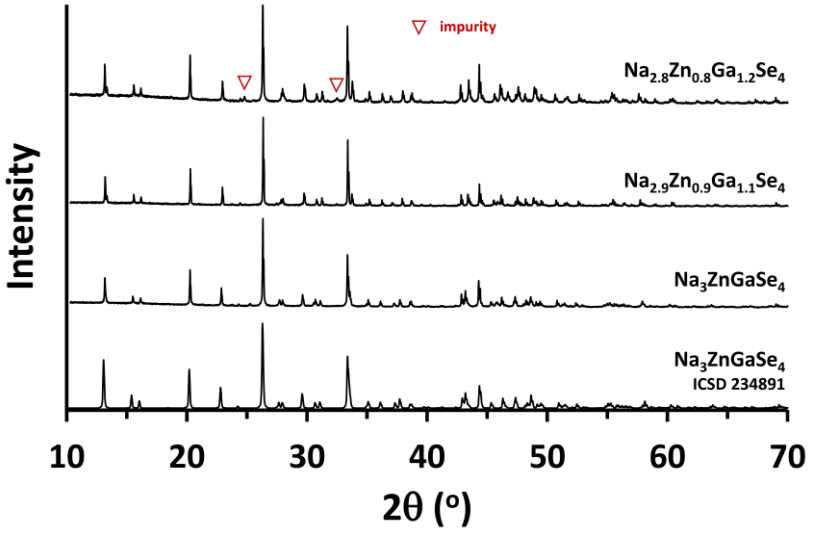

Figure S6. Comparison of XRD patterns of $Na_{3-x}Zn_xGa_{1+x}Se_4$.

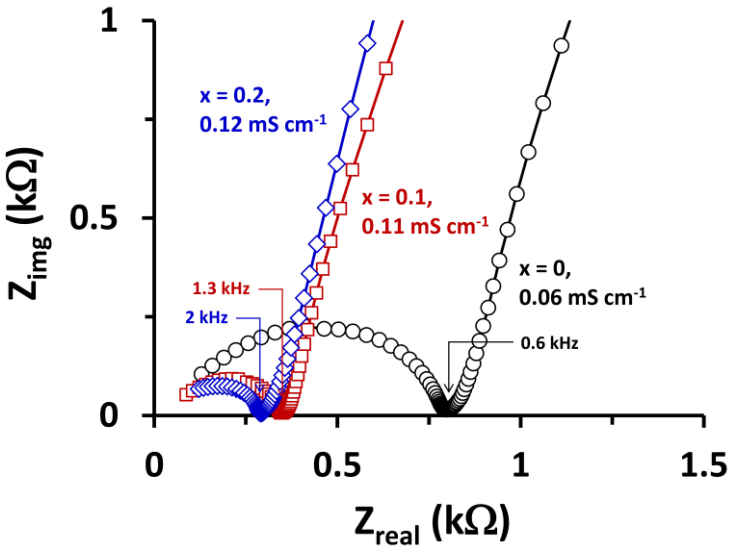

Figure S7. EIS spectra of $Na_{3-x}Zn_xGa_{1+x}Se_4$. In contrast to the conspicuous enhancement of σ_{ion} upon incorporating vacancies in $Na_{3-x}Zn_xGa_{1+x}S_4$, the σ_{ion} was increased only by two-fold due to the pre-existing vacancies in $Na_3ZnGaSe_4$.

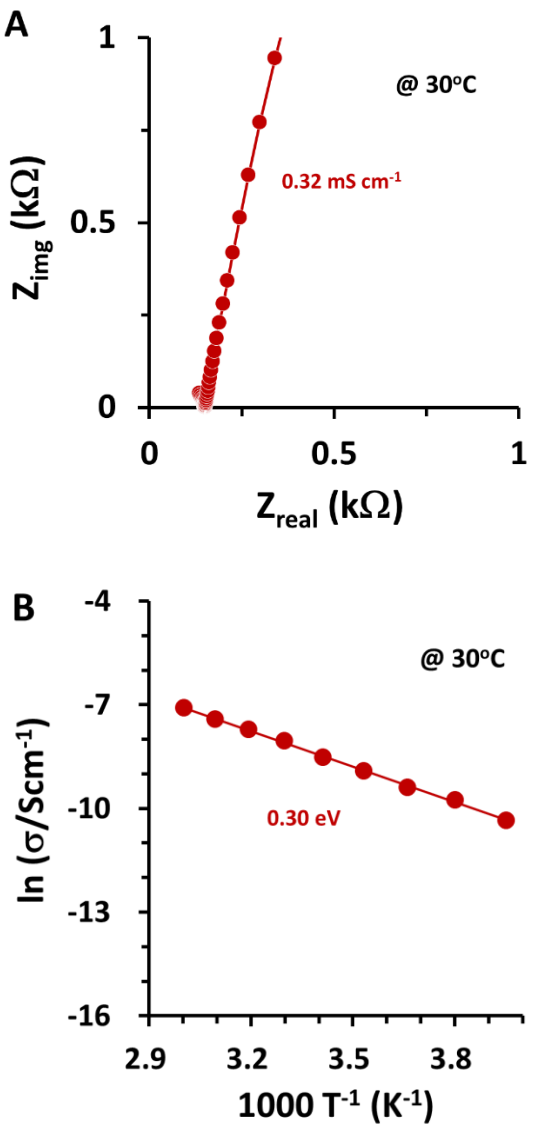

Figure S8. (A) EIS spectrum and (B) Arrhenius plot for a hot-pressed (200°C, 5T, 10 min) pellet of $Na_{2.8}Zn_{0.8}Ga_{1.2}S_4$.

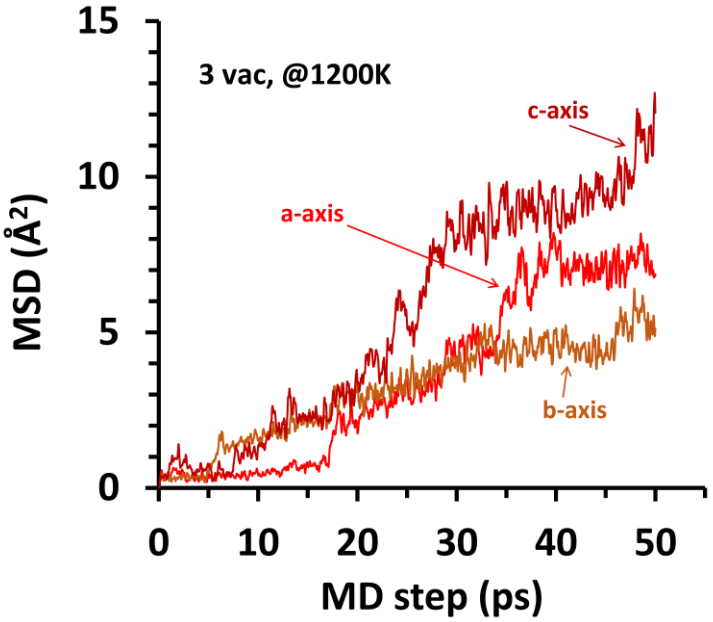

Figure S9. Difference in MSD plots along the axis directions in 3 vac ($Na_{2.81}Zn_{0.81}Ga_{1.19}S_4$).

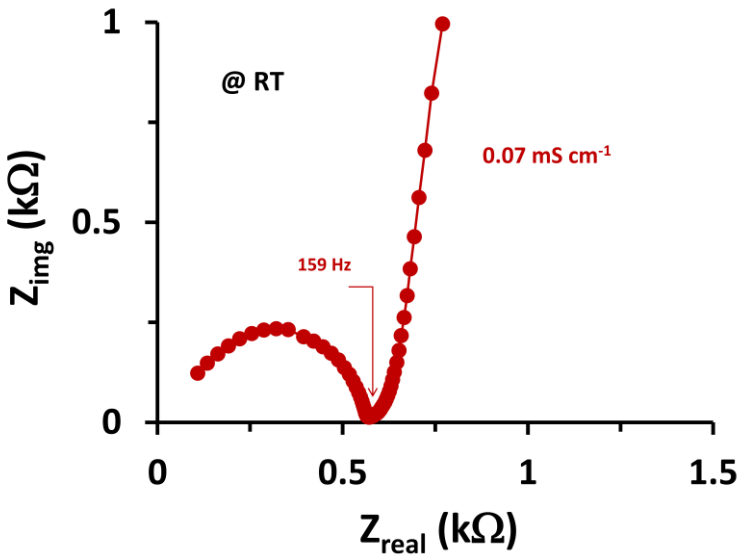

Figure S10. EIS spectrum for $Na_{2.8}Zn_{0.8}Ga_{1.2}S_4$ after drying at 80°C. The resistance of 0.57 kΩ was quite close to 0.55 kΩ measured with as-made $Na_{2.8}Zn_{0.8}Ga_{1.2}S_4$ (Figure 4A).

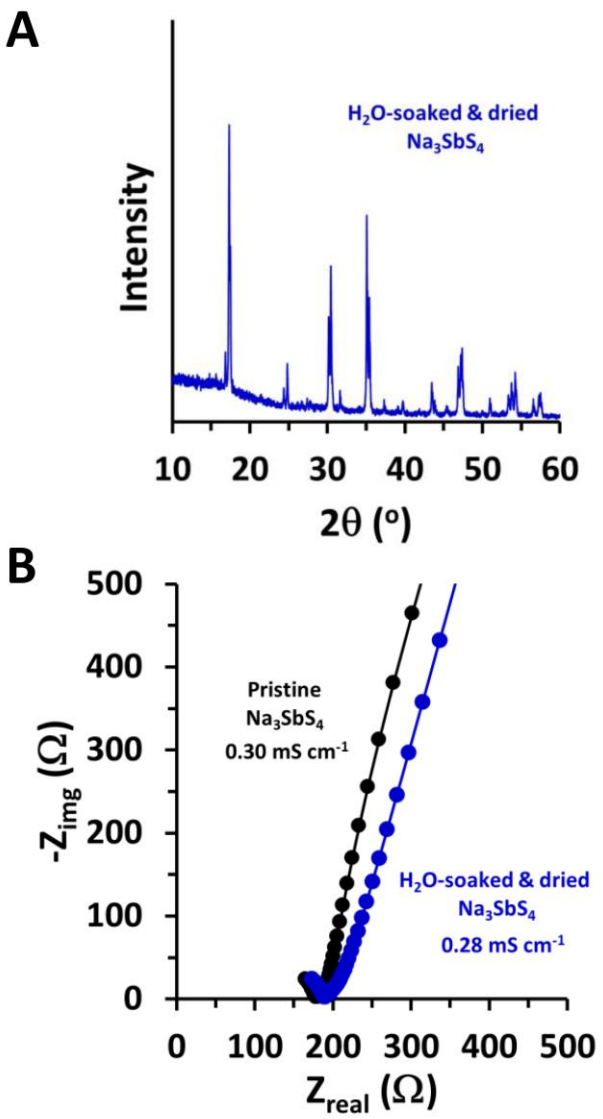

Figure S11. (A) Recovery of XRD patterns of Na_3SbSe_4 after vacuum-drying at 150°C. (B) Comparison of EIS spectra before and after soaking in water. Despite the sign of reactions in water (possibly, excessive hydration beyond $Na_3SbS_4 \cdot 9H_2O$), the crystalline structure and the ionic conductivity were not altered after vacuum-drying.

Table S1: Rietveld refinement results of Na_3ZnGaS_4.

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{iso} ($Å^2$)	SOF
Na1	16f	0.1165(3)	0.6335(3)	-0.125	0.018(2)	1
Na2	32g	0.1295(4)	0.9084(4)	-0.0149(3)	0.045(2)	1
Ga1	32g	0.12295(12)	0.67012(12)	0.06197(10)	0.0039(5)	0.5
Zn1	32g	0.12295(12)	0.67012(12)	0.06197(10)	0.0039(5)	0.5
S1	16e	0.25	0.5795(4)	0	0.0052(15)	1
S2	32g	0.0483(2)	0.5359(3)	0.12683(19)	0.0090(12)	1
S3	16d	0	0.75	-0.0161(2)	0.0086(15)	1

Space group: $I4_1/acd$
Number of formula per unit cell (z) = 16
Lattice parameters: a =12.96673(5) Å, c = 18.5662(1) Å
Agreement factors: R_p = 7.01, R_{wp} = 9.12, R_{exp} = 7.48, and χ^2 = 1.49

Table S2: Rietveld refinement results of $Na_{2.95}Zn_{0.95}Ga_{1.05}S_4$.

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{iso} ($Å^2$)	SOF
Na1	16f	0.1167(3)	0.6333(3)	-0.125	0.012(3)	1.000(8)
Na2	32g	0.1299(4)	0.9098(4)	-0.0165(3)	0.048(2)	0.975(5)
Ga1	32g	0.12312(13)	0.67064(13)	0.06141(11)	0.0011(5)	0.525
Zn1	32g	0.12312(13)	0.67064(13)	0.06141(11)	0.0011(5)	0.475
S1	16e	0.25	0.5794(4)	0	0.0012(16)	1
S2	32g	0.0472(3)	0.5344(3)	0.1267(2)	0.0067(14)	1
S3	16d	0	0.75	-0.0179(2)	0.0023(16)	1

Space group: $I4_1/acd$
Number of formula per unit cell (z) = 16
Lattice parameters: a =12.9367(1) Å, c = 18.5920(3) Å
Agreement factors: R_p = 7.00, R_{wp} = 8.97, R_{exp} = 7.71, and χ^2 = 1.35

Table S3: Rietveld refinement results of $Na_{2.90}Zn_{0.90}Ga_{1.10}S_4$.

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{iso} (Å^2)	SOF
Na1	16f	0.1167(5)	0.6333(5)	-0.125	0.009(4)	1.000(12)
Na2	32g	0.1333(6)	0.9126(6)	-0.0156(4)	0.047(4)	0.950(6)
Ga1	32g	0.12339(18)	0.66970(18)	0.06162(16)	0.0081(7)	0.55
Zn1	32g	0.12339(18)	0.66970(18)	0.06162(16)	0.0081(7)	0.45
S1	16e	0.25	0.5804(6)	0	0.006(2)	1
S2	32g	0.0468(4)	0.5341(4)	0.1273(3)	0.0058(18)	1
S3	16d	0	0.75	-0.0190(4)	0.025(3)	1

Space group: $I4_1/acd$
Number of formula per unit cell (z) = 16
Lattice parameters: a =12.9249(2) Å, c = 18.6266(4) Å
Agreement factors: R_p = 8.71, R_{wp} = 11.2, R_{exp} = 10.06, and χ^2 = 1.24

Table S4: Rietveld refinement results of $Na_{2.85}Zn_{0.85}Ga_{1.15}S_4$.

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{iso} (Å^2)	SOF
Na1	16f	0.1168(3)	0.6332(3)	-0.125	0.017(3)	1.000(9)
Na2	32g	0.1328(5)	0.9098(5)	-0.0173(3)	0.062(3)	0.925(5)
Ga1	32g	0.12302(12)	0.67100(12)	0.06137(11)	0.0080(4)	0.575
Zn1	32g	0.12302(12)	0.67100(12)	0.06137(11)	0.0080(4)	0.425
S1	16e	0.25	0.5812(4)	0	0.0065(15)	1
S2	32g	0.0469(3)	0.5359(3)	0.1271(2)	0.0123(13)	1
S3	16d	0	0.75	-0.0175(2)	0.0185(17)	1

Space group: $I4_1/acd$
Number of formula per unit cell (z) = 16
Lattice parameters: a =12.9021(1) Å, c = 18.6597(2) Å
Agreement factors: R_p = 6.78, R_{wp} = 8.76, R_{exp} = 7.76, and χ^2 = 1.27

Table 5: Rietveld refinement results of $Na_{2.80}Zn_{0.80}Ga_{1.20}S_4$.

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{iso} (Å^2)	SOF
Na1	16f	0.1175(5)	0.6325(5)	-0.125	0.017(4)	0.983(12)
Na2	32g	0.1321(6)	0.9104(6)	-0.0177(4)	0.059(4)	0.909(6)
Ga1	32g	0.12328(17)	0.67121(17)	0.06096(14)	0.0040(5)	0.6
Zn1	32g	0.12328(17)	0.67121(17)	0.06096(14)	0.0040(5)	0.4
S1	16e	0.25	0.5810(5)	0	0.005(2)	1
S2	32g	0.0482(3)	0.5355(3)	0.1270(3)	0.0062(17)	1
S3	16d	0	0.75	-0.0175(3)	0.015(2)	1

Space group: *$I4_1/acd$*
Number of formula per unit cell (z) = 16
Lattice parameters: a =12.8849(2) Å, c = 18.6855(4) Å
Agreement factors: R_p = 8.64, R_{wp} = 11.2, R_{exp} = 10.23, and χ^2 = 1.20

Table S6: Rietveld refinement results of $Na_{2.70}Zn_{0.70}Ga_{1.30}S_4$.

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{iso} (Å^2)	SOF
Na1	16f	0.1139(5)	0.6361(5)	-0.125	0.039(5)	0.979(12)
Na2	32g	0.1361(6)	0.9108(6)	-0.0169(5)	0.064(4)	0.860(6)
Ga1	32g	0.12274(16)	0.67179(16)	0.06108(14)	0.0018(6)	0.65
Zn1	32g	0.12274(16)	0.67179(16)	0.06108(14)	0.0018(6)	0.35
S1	16e	0.25	0.5829(5)	0	0.000(2)	1
S2	32g	0.0463(3)	0.5359(3)	0.1274(3)	0.0012(17)	1
S3	16d	0	0.75	-0.0176(3)	0.014(2)	1

Space group: *$I4_1/acd$*
Number of formula per unit cell (z) = 16
Lattice parameters: a =12.8320(2) Å, c = 18.7777(4) Å
Agreement factors: R_p = 7.89, R_{wp} = 10.2, R_{exp} = 9.15, and χ^2 = 1.26

Table S7: Rietveld refinement results of $Na_{2.60}Zn_{0.60}Ga_{1.40}S_4$. Due to the presence of $NaGaS_2$ impurities, the total amount of Na was assumed to be 2.70 and all the vacancies were placed on Na(2) sites.

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{iso} (Å^2)	SOF
Na1	16f	0.1097(6)	0.6403(6)	-0.125	0.022(5)	1
Na2	32g	0.1318(8)	0.9121(8)	-0.0127(5)	0.044(4)	0.85
Ga1	32g	0.1235(2)	0.6709(2)	0.06049(19)	0.0202(10)	0.65
Zn1	32g	0.1235(2)	0.6709(2)	0.06049(19)	0.0202(10)	0.35
S1	16e	0.25	0.5761(7)	0	0.002(3)	1
S2	32g	0.0491(5)	0.5353(4)	0.1288(4)	0.016(3)	1
S3	16d	0	0.75	-0.0166(4)	0.045(4)	1

Space group: $I4_1/acd$
Number of formula per unit cell (z) = 16
Lattice parameters: a =12.8310(2) Å, c = 18.7793(6) Å
Agreement factors: R_p = 8.23, R_{wp} = 10.8, R_{exp} = 10.09 and χ^2 = 1.14

Table S8: Rietveld refinement results of $Na_{2.50}Zn_{0.50}Ga_{1.50}S_4$. Due to the presence of $NaGaS_2$ impurities, the total amount of Na was assumed to be 2.70 and all the vacancies were placed on Na(2) sites.

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{iso} (Å^2)	SOF
Na1	16f	0.1056(8)	0.6444(8)	-0.125	0.027(8)	1
Na2	32g	0.1253(10)	0.9152(10)	-0.0115(7)	0.004(5)	0.85
Ga1	32g	0.1240(4)	0.6693(3)	0.0603(3)	0.036(2)	0.75
Zn1	32g	0.1240(4)	0.6693(3)	0.0603(3)	0.036(2)	0.25
S1	16e	0.25	0.5758(11)	0	0.003(5)	1
S2	32g	0.0498(7)	0.5328(6)	0.1317(5)	0.017(4)	1
S3	16d	0	0.75	-0.0152(6)	0.059(8)	1

Space group: $I4_1/acd$
Number of formula per unit cell (z) = 16
Lattice parameters: a =12.8297(3) Å, c = 18.7836(8) Å
Agreement factors: R_p = 8.70, R_{wp} = 11.4, R_{exp} = 10.04 and χ^2 = 1.28