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Supplementary Information

Nominally stoichiometric $Na_3(W_xSi_xSb_{1-2x})S_4$ as a superionic solid electrolyte

Suyeon Han,‡[a] Jung Yong Seo,‡[a] Woon Bae Park,*[a] S. J. Richard Prabakar,[a] Sangwon Park,[a] Kee-Sun Sohn*[b] and Myoungho Pyo*[a]

[a.] *Department of Advanced Components and Materials Engineering, Sunchon National University, Chonnam 57922, Republic of Korea E-mail: wbpark@scnu.ac.kr (W. B. Park), mho@sunchon.ac.kr (M. Pyo)*

[b.] *Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 05006, Republic of Korea. kssohn@sejong.ac.kr*

‡ These two authors contributed equally to the work

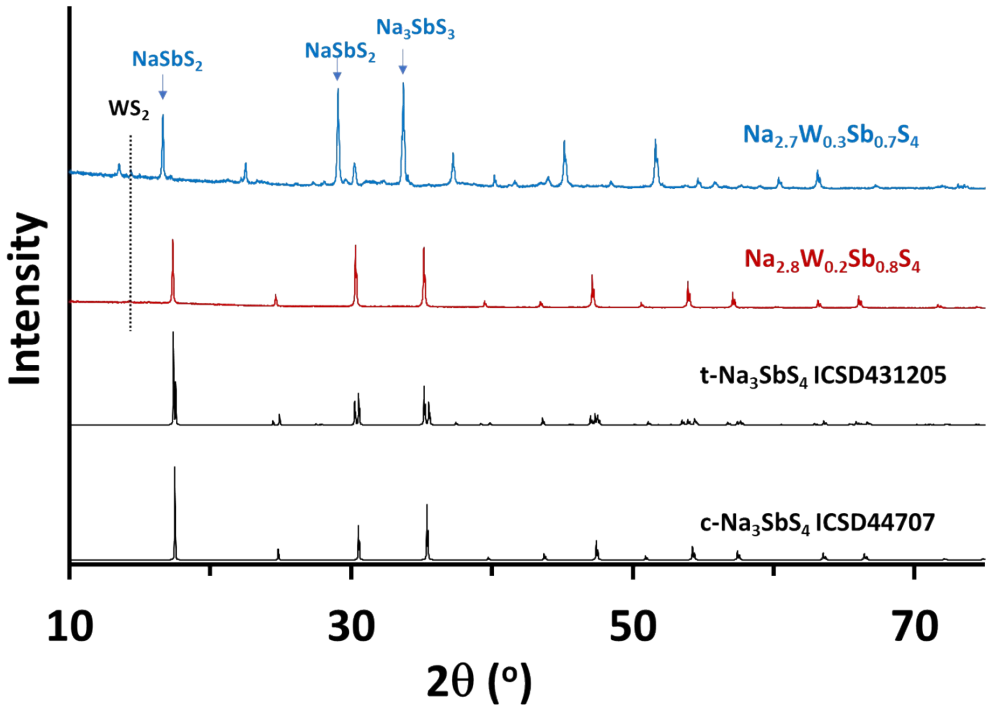
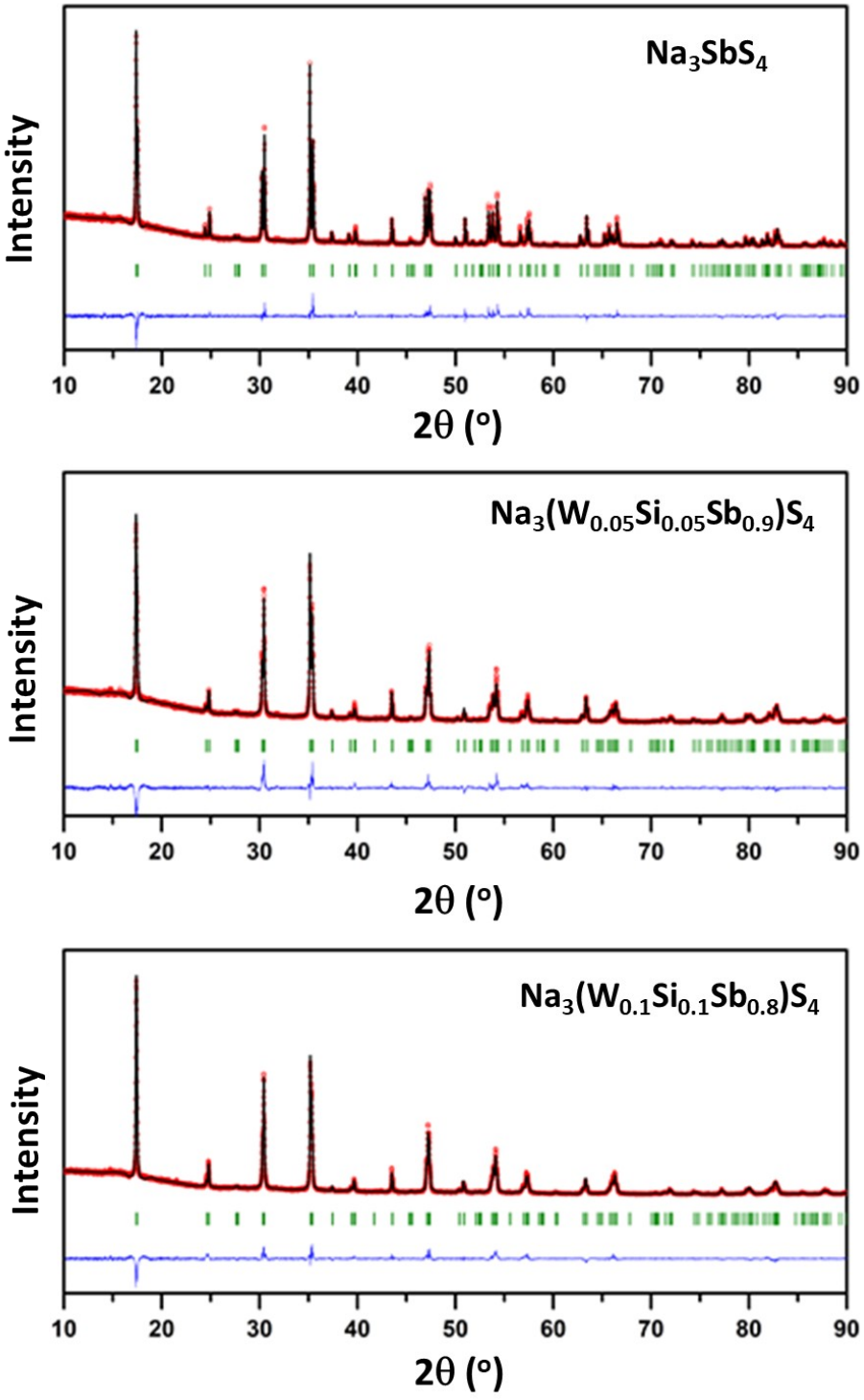


Fig. S1 XRD patterns of $Na_{2.8}W_{0.2}Sb_{0.8}S_4$ and $Na_{2.8}W_{0.2}Sb_{0.8}S_4$. The presence of small amounts of WS_2 and Na_nSbS_m impurities are noticeable.


Na3SbS4
Intensity
10
20
30
40
50
60
70
80
90
2θ (°)
Na3(W0.05Si0.05Sb0.9)S4
Intensity
10
20
30
40
50
60
70
80
90
2θ (°)
Na3(W0.1Si0.1Sb0.8)S4
Intensity
10
20
30
40
50
60
70
80
90
2θ (°)

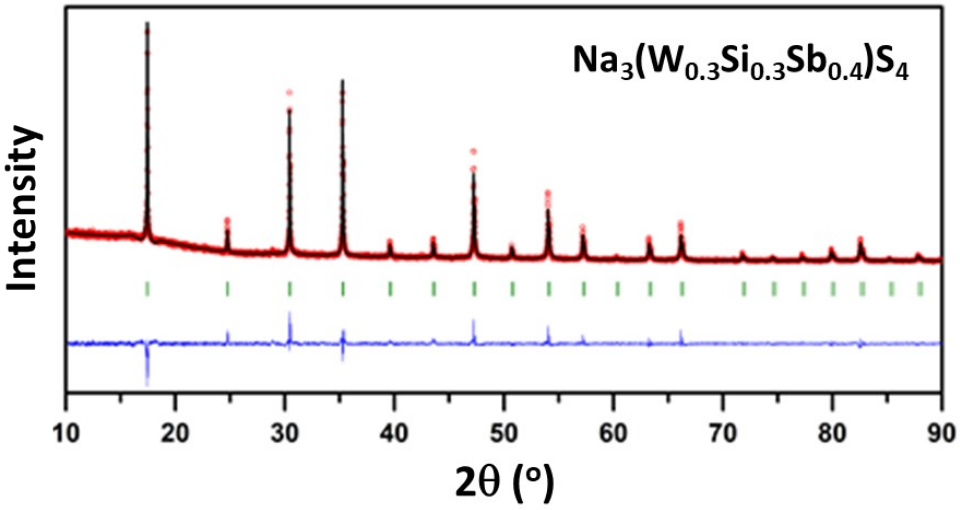


Fig. S2 Full pattern Rietveld refinement fits obtained using either *P*-42$_1$*c* or *I*-43*m* space groups. In the figure, experimental, calculated, and difference profiles are shown by red dots and by black and blue lines, respectively. The vertical tick marks above the difference profile denote the position of Bragg reflections. For the Rietveld fit of $Na_3(W_{0.2}Si_{0.2}Sb_{0.6})$, see the text.

Table S1

Atomic coordinate and site occupancy factor (SOF) of Na_3SbS_4.

Atom	Wyckoff symbol	x/a	y/b	z/c	U (Å^2)	SOF
Na	4d	0	0.5	0.4363(8)	0.040(3)	1.0
Na	2b	0	0	0.5	0.043(3)	1.0
Sb	2a	0	0	0	0.018(1)	1.0
S	8e	0.2899(6)	0.3215(6)	0.6914(5)	0.022(1)	1.0

Space group: *P*-42$_1$*c*
Number of formula per unit cell (z) = 2
Lattice parameters: a =7.1649(1) Å, c = 7.2979(1) Å, α = β = γ =90°
Agreement factors: R_p = 7.20, R_{wp} = 10.2, R_{exp} = 6.10 and χ^2 = 2.82

Table S2

Atomic coordinate and site occupancy factor (SOF) of $Na_3(W_{0.05}Si_{0.05}Sb_{0.9})S_4$.

Atom	Wyckoff symbol	x/a	y/b	z/c	U (Å^2)	SOF
Na	4d	0	0.5	0.4423(10)	0.041(3)	1.0
Na	2b	0	0	0.5	0.037(4)	1.0
Sb	2a	0	0	0	0.016(1)	0.9
Si	2a	0	0	0	0.016(1)	0.05
W	2a	0	0	0	0.016(1)	0.05
S	8e	0.2967(7)	0.3174(6)	0.6940(5)	0.015(1)	1.0

Space group: *P*-42$_1$c
Number of formula per unit cell (z) = 2
Lattice parameters: a =7.1711(1) Å, c = 7.2612(2) Å, $\alpha = \beta = \gamma = 90°$
Agreement factors: R_p = 6.88, R_{wp} = 11.5, R_{exp} = 6.01 and χ^2 = 3.09

Table S3

Atomic coordinate and site occupancy factor (SOF) of $Na_3(W_{0.1}Si_{0.1}Sb_{0.8})S_4$.

Atom	Wyckoff symbol	x/a	y/b	z/c	U (Å^2)	SOF
Na	4d	0	0.5	0.4435(13)	0.101(4)	1.0
Na	2b	0	0	0.5	0.085(5)	1.0
Sb	2a	0	0	0	0.039(1)	0.8
Si	2a	0	0	0	0.039(1)	0.1
W	2a	0	0	0	0.039(1)	0.1
S	8e	0.2986(6)	0.3232(5)	0.6931(5)	0.049(1)	1.0

Space group: *P*-42$_1$*c*
Number of formula per unit cell (z) = 2
Lattice parameters: a =7.1795(1) Å, c = 7.2411(1) Å, $\alpha = \beta = \gamma = 90°$
Agreement factors: R_p = 6.26, R_{wp} = 8.38, R_{exp} = 5.20 and χ^2 = 2.60

Table S4

Atomic coordinate and site occupancy factor (SOF) of $Na_3(W_{0.2}Si_{0.2}Sb_{0.6})S_4$.

Atom	Wyckoff symbol	x/a	y/b	z/c	U (Å^2)	SOF
Na	6b	0	0	0.5	0.048(3)	0.84(3)
Na	12d	0.75	0.5	0	0.10(6)	0.078(16)
Sb	2a	0	0	0	0.025(1)	0.6
Si	2a	0	0	0	0.025(1)	0.2
W	2a	0	0	0	0.025(1)	0.2
S	8c	0.1885(6)	0.1885(6)	0.1885(6)	0.048(3)	1.0

Space group: *I*-43*m*
Number of formula per unit cell (z) = 2
Lattice parameters: a =7.1997(1) Å, $\alpha = \beta = \gamma = 90°$
Agreement factors: R_p = 8.61, R_{wp} = 11.3, R_{exp} = 10.14 and χ^2 = 1.24

Table S5

Atomic coordinate and site occupancy factor (SOF) of $Na_3(W_{0.3}Si_{0.3}Sb_{0.4})S_4$.

Atom	Wyckoff symbol	x/a	y/b	z/c	U (Å^2)	SOF
Na	6b	0	0	0.5	0.332(5)	0.813(19)
Na	12d	0.75	0.5	0	0.37(3)	0.094(9)
Sb	2a	0	0	0	0.265(1)	0.4
Si	2a	0	0	0	0.265(1)	0.3
W	2a	0	0	0	0.265(1)	0.3
S	8c	0.1879(4)	0.1879(4)	0.1879(4)	0.296(1)	1.0

Space group: *I*-43*m*
Number of formula per unit cell (z) = 2
Lattice parameters: a =7.1932(1) Å, $\alpha = \beta = \gamma = 90°$
Agreement factors: R_p = 7.29, R_{wp} = 9.80, R_{exp} = 7.63 and χ^2 = 1.65

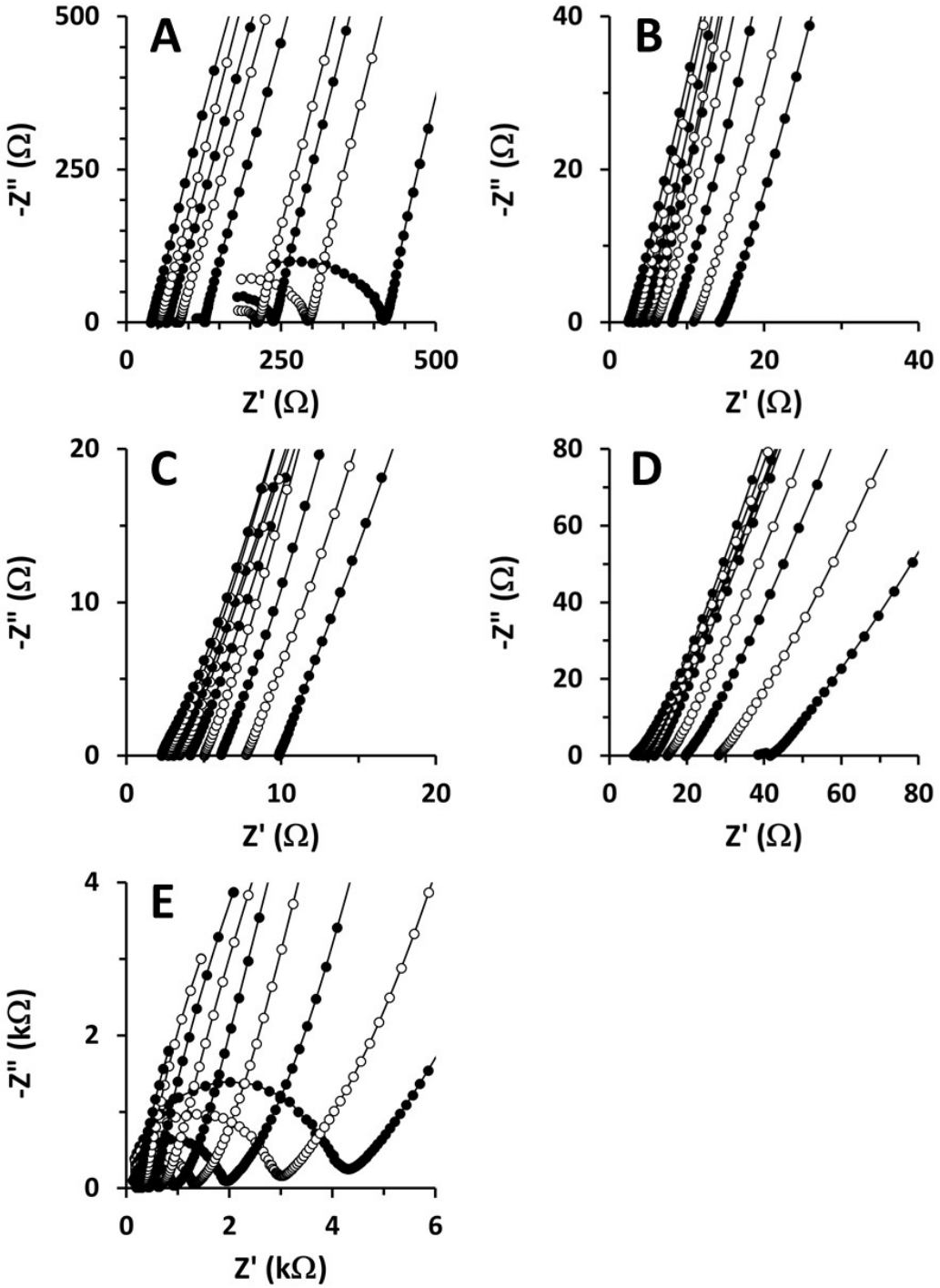


Fig. S3 EIS spectra at various temperature between -20 and +60 °C for (A) x = 0, (B) x = 0.1, (C) x = 0.2, (D) x = 0.3, and (E) x = 0.4 in $Na_3(W_xSi_xSb_{1-2x})S_4$.