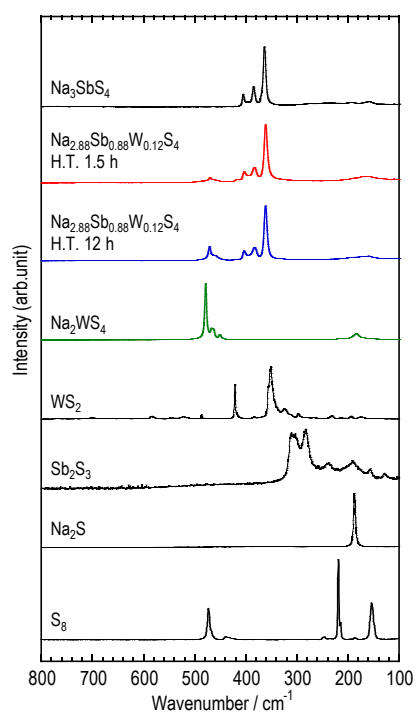


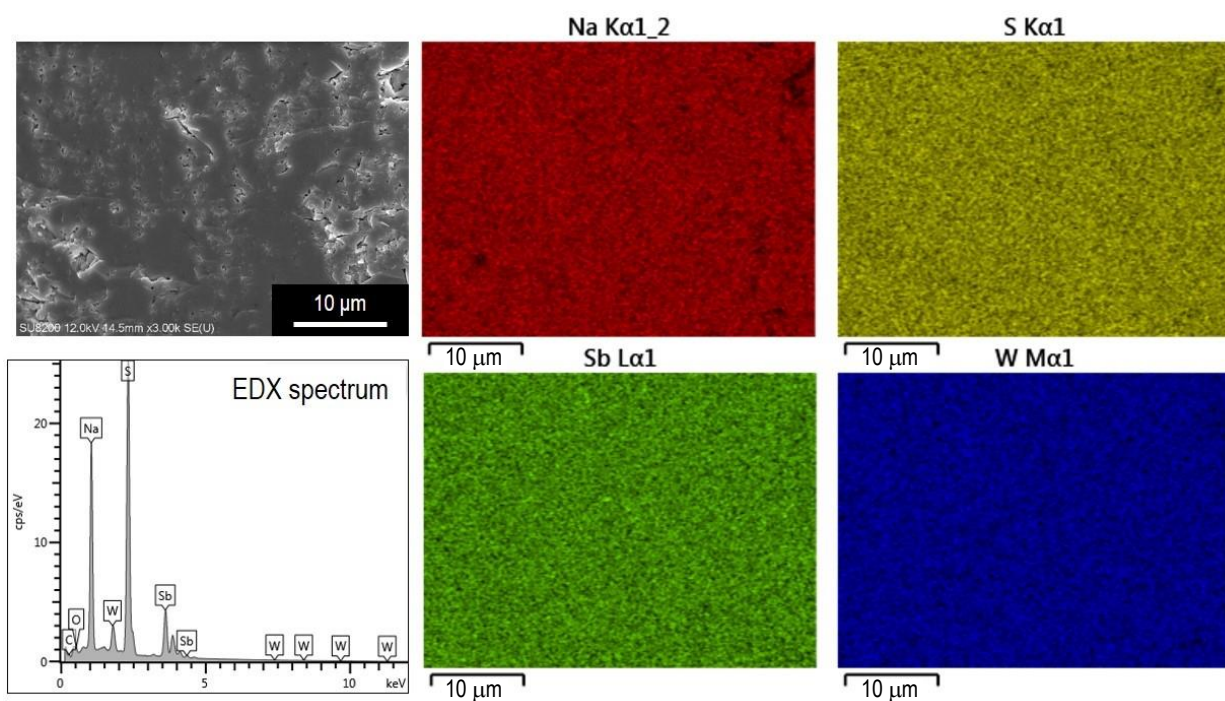
Supplementary Information

**A sodium-ion sulfide solid electrolyte with unprecedented conductivity
at room temperature**

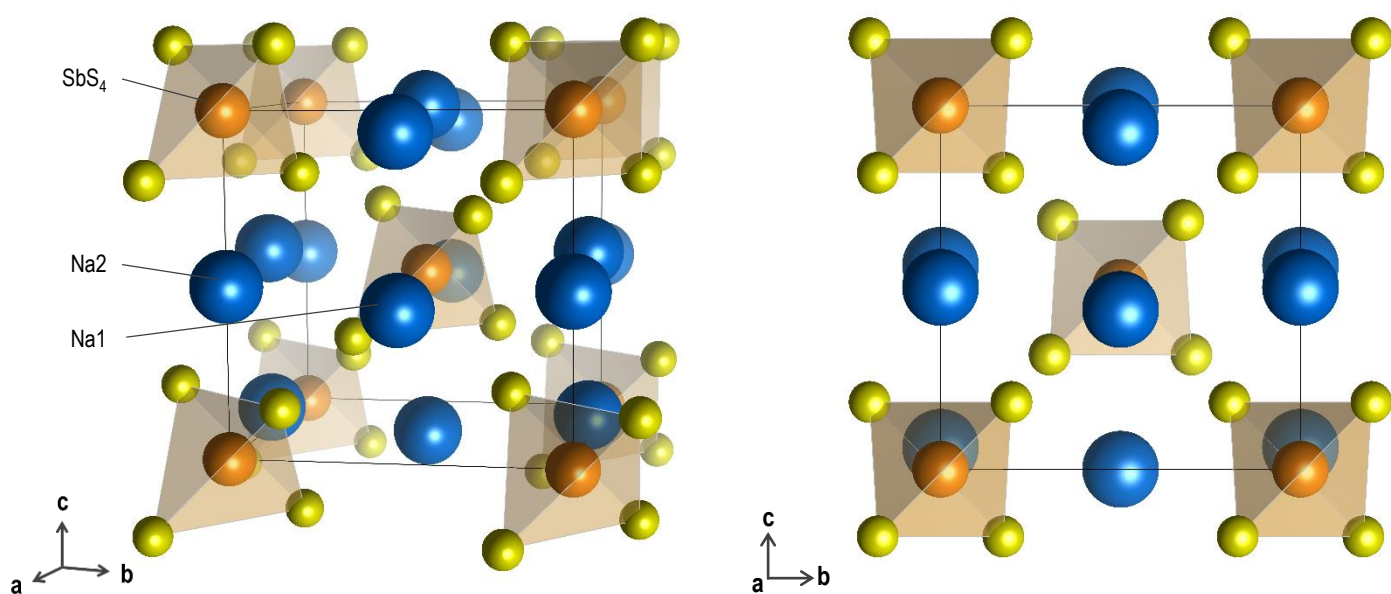
A. Hayashi *et al.*



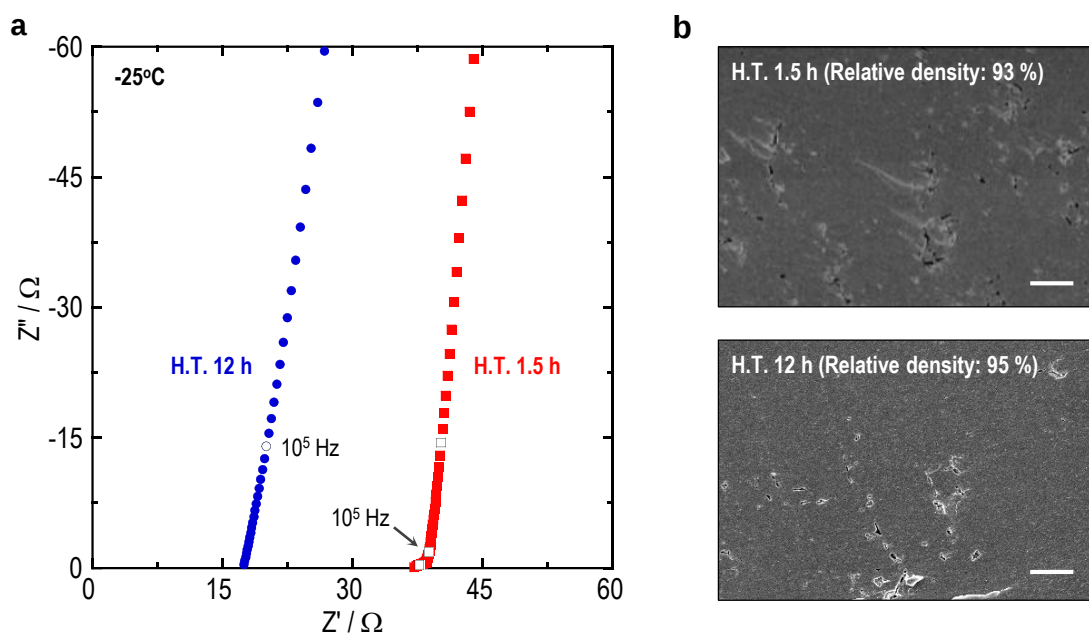
Supplementary Figure 1 Raman spectra of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ and its starting materials.



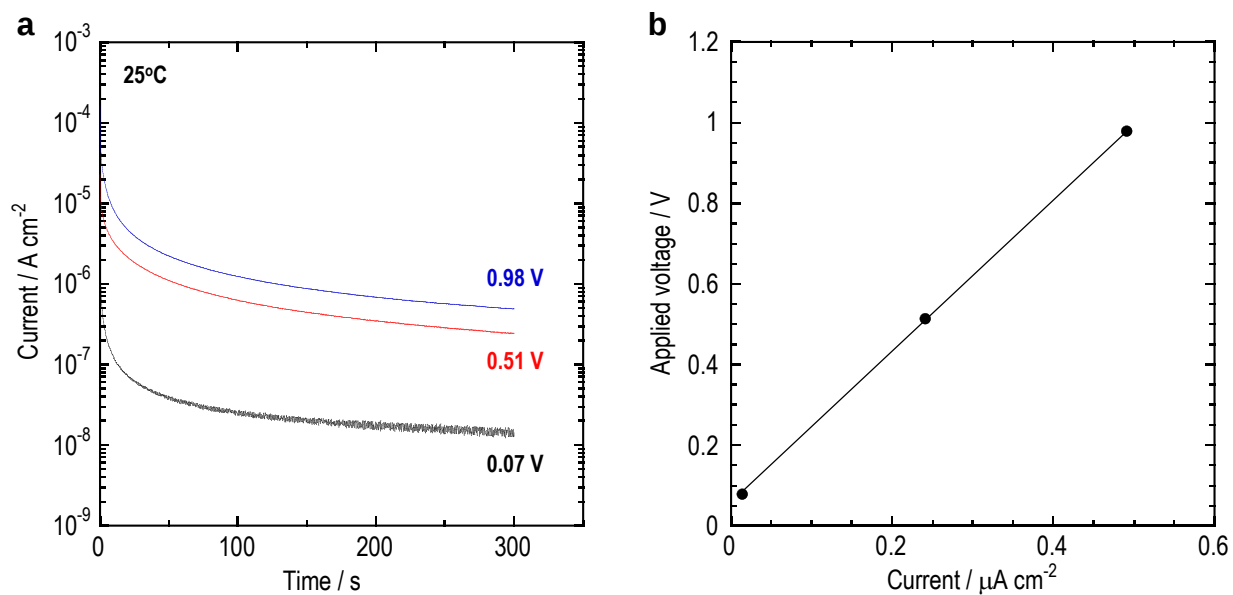
Supplementary Figure 2 SEM image and EDX mappings of Na, S, Sb, and W for the cross-section of a $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ pellet.



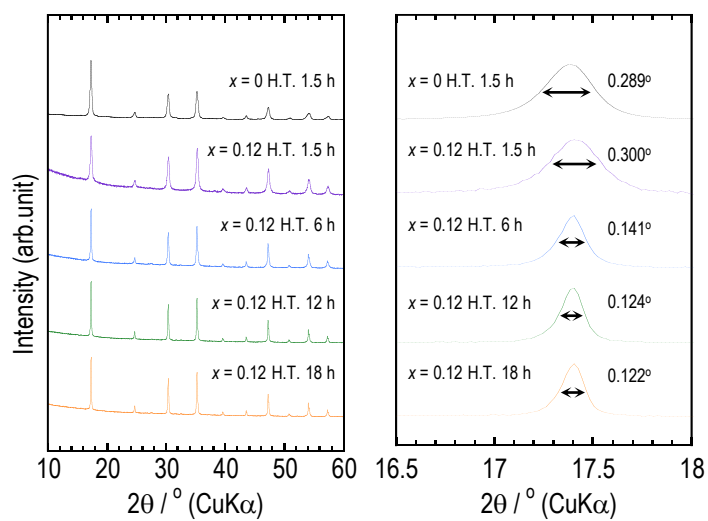
Supplementary Figure 3 Crystal structure of tetragonal Na_3SbS_4 ($x = 0$) with the unit cell outlined. The Na, Sb, and S sites are represented by blue, orange, and yellow balls, respectively. Na is arranged in a zigzag manner, and the Sb_4 tetrahedra is slightly distorted.



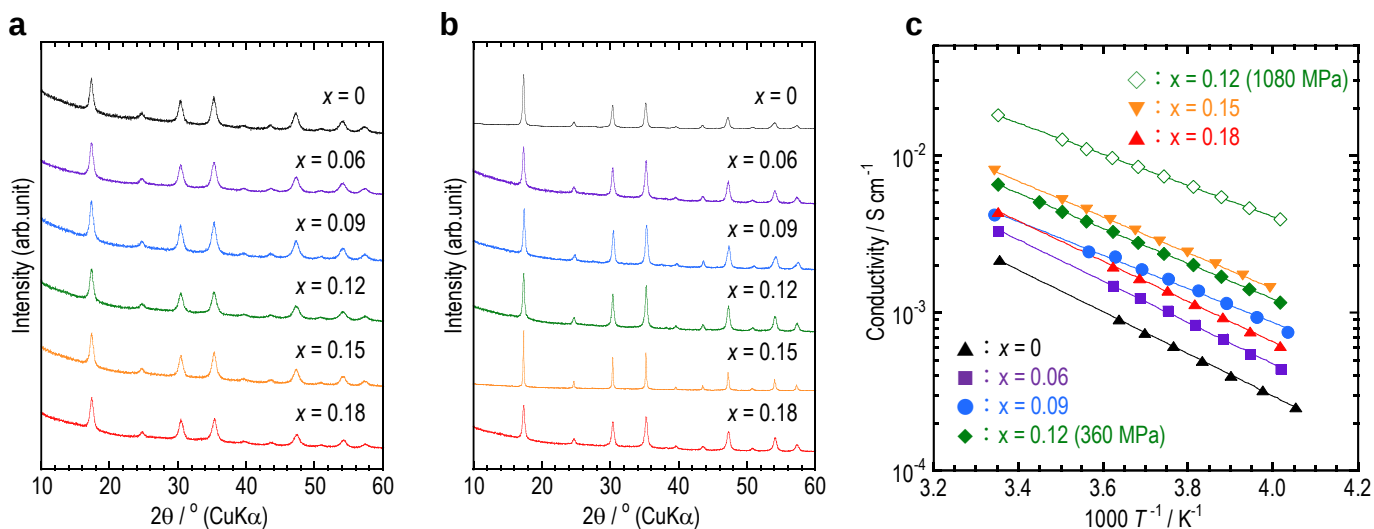
Supplementary Figure 4 Evaluation of electrical conductivity for $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$. (a) Nyquist plots at $-25\text{ }^{\circ}\text{C}$ for the $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ pellets heated for 1.5 and 12 h. (b) Cross-sectional SEM images of the pellets. Scale bar is $2\text{ }\mu\text{m}$ for the top panel and $1\text{ }\mu\text{m}$ for the bottom panel.



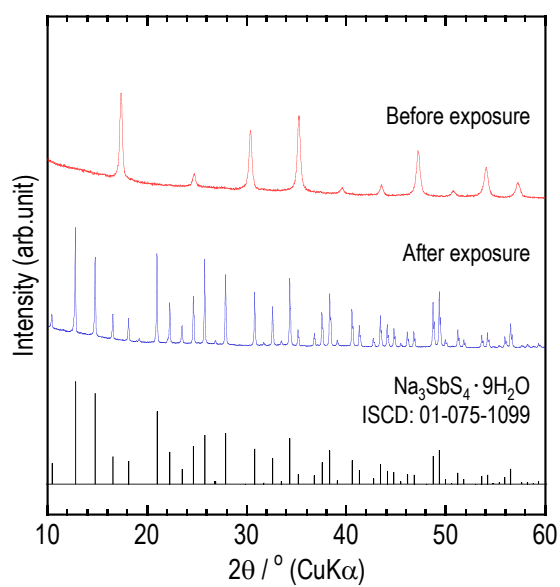
Supplementary Figure 5 Evaluation of electronic conductivity for Na_{2.88}Sb_{0.88}W_{0.12}S₄. (a) DC polarization curves for Na_{2.88}Sb_{0.88}W_{0.12}S₄ under the applied voltage of 0.07–0.98 V at 25 °C. (b) The relationship between the applied voltage and constant current is also shown.



Supplementary Figure 6 XRD patterns of $\text{Na}_{3-x}\text{Sb}_{1-x}\text{W}_x\text{S}_4$ electrolytes prepared by heat treatment (H.T.) for different durations. Full-width at half maximum (FWHM) of the most intense peak is denoted in the right panel.



Supplementary Figure 7 XRD pattern and conductivity for the $\text{Na}_{3-x}\text{Sb}_{1-x}\text{W}_x\text{S}_4$ electrolytes prepared under different experimental conditions. (a) XRD patterns of milled $\text{Na}_{3-x}\text{Sb}_{1-x}\text{W}_x\text{S}_4$ samples and (b) those of the heat-treated $\text{Na}_{3-x}\text{Sb}_{1-x}\text{W}_x\text{S}_4$ samples. Heat treatment was carried out at 275 °C for 1.5 h for the milled samples pelletized with a molding pressure of 360 MPa. Temperature-dependence of the conductivity of the heat-treated pellets (b) is shown in panel (c). The Arrhenius plot for the pellet prepared with a molding pressure of 1080 MPa, followed by heating at 275 °C for 1.5 h is also displayed.



Supplementary Figure 8 XRD patterns of $\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ electrolytes before and after exposure to humid air for 1.5 h.

Supplementary Table 1 Crystallographic data for the prepared Na_{2.88}Sb_{0.88}W_{0.12}S₄.

Crystal System	Cubic	Lattice Parameter	$a = 7.1921(1) \text{ \AA}$			
Space Group	$I \bar{4}3m$ (No. 217)	Volume, Z	$V = 372.02 \text{ \AA}^3, Z = 2$			
Atoms	Wyckoff	Occ.	x	y	z	$B / \text{\AA}^2$
Na	6b	0.974 (2)	0	1/2	1/2	6.682
Sb	2a	0.922 (5)	0	0	0	0.984
W	2a	0.078 (5)	0	0	0	= $B(\text{Sb})$
S	8c	1	0.1851(1)	0.1851(1)	0.1851(1)	1.909

* $R_{\text{wp}} = 0.0240, R_{\text{p}} = 0.0182, R_{\text{e}} = 0.0140, S = R_{\text{wp}}/R_{\text{e}} = 1.71$

Supplementary Table 2 Crystallographic data for the prepared Na₃SbS₄.

Crystal System	Tetragonal		Lattice Parameter	$a = 7.1708(12) \text{ \AA}$ $c = 7.2376(2) \text{ \AA}$		
Space Group	$P \bar{4}2_1c$ (No.114)		Volume, Z	$V = 372.16 \text{ \AA}^3$, $Z = 2$		
Atoms	Wyckoff	Occ.	x	y	z	B / $\text{\AA}^2$
Na 1	$4d$	1	0	1/2	0.4396(5)	4.50(12)
Na 2	$2b$	1	0	0	1/2	4.6(2)
Sb	$2a$	1	0	0	0	1.13(2)
S	$8e$	1	0.3029(3)	0.3255(3)	0.6848(2)	1.82(4)

* $R_{\text{wp}} = 0.0245$, $R_{\text{p}} = 0.0177$, $R_{\text{e}} = 0.0124$, $S = R_{\text{wp}}/R_{\text{e}} = 1.98$

Supplementary Table 3 Conductivity at 25 °C (σ_{25}) and activation energy (E_a) for conduction of the $\text{Na}_{3-x}\text{Sb}_{1-x}\text{W}_x\text{S}_4$ pellets prepared by cold-pressing at 360 MPa, followed by heat treatment at 275 °C for 1.5 hours.

$\text{Na}_{3-x}\text{Sb}_{1-x}\text{W}_x\text{S}_4$	$\sigma_{25} / \text{S cm}^{-1}$	$E_a / \text{kJ mol}^{-1}$
$x = 0$	2.1×10^{-3}	26
$x = 0.06$	3.4×10^{-3}	25
$x = 0.09$	4.4×10^{-3}	21
$x = 0.12$	6.4×10^{-3}	21
$x = 0.15$	7.7×10^{-3}	22
$x = 0.18$	4.5×10^{-3}	24