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# **Supplementary Information**

# Aqueous Solution Synthesis of Na<sub>3</sub>SbS<sub>4</sub>-Na<sub>2</sub>WS<sub>4</sub> Superionic Conductors

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Fig. S1 Amounts of  $H_2S$  gas as a function of time for the Na<sub>2</sub>S solid powder and Na<sub>2</sub>S aqueous solution, normalised by sulfur in the samples. The humidity during measurement for Na<sub>2</sub>S solid powder was 50%. The concentration and pH of Na<sub>2</sub>S aqueous solution were 10 wt.% and 13.7, respectively.







#### Fig. S2 Photographic images of the precursor aqueous solutions of (a) $Na_3SbS_4$ and (b) $Na_2WS_4$ .

(a)







Wavenumber / cm<sup>-1</sup>

Fig. S3 (a) Photographic image of the decomposition product prepared by adding HCl into the precursor aqueous solution of  $Na_3SbS_4$  and subsequent drying at 150 °C. (b) Raman spectra of the decomposition product,  $Na_3SbS_4$ ,  $Sb_2S_3$ , and sulfur.



Outermost surface 1 nm 5 nm



Fig. S4 (a)  $C_{1s}$ , (b)  $S_{2p}$ , (c)  $Na_{1s}$ , and (d)  $O_{1S}$  and  $Sb_{3d}$  photoelectron spectra of the  $Na_3SbS_4$  prepared by a liquid-phase technique with drying at 150 °C. The observed binding energies were calibrated with respect to adventitious C1s peak at 284.7 eV. The peaks of  $SbS_4$  were broadened during etching.



Fig. S5 Rietveld refinement profiles of X-ray powder diffraction data for  $Na_3SbS_4$  prepared by a liquid-phase technique with drying at 150 °C recorded at room temperature. Red dots and light blue line denote the observed and calculated XRD patterns, respectively. The green sticks mark the position of the reflections for  $Na_3SbS_4$ . The difference between the observed and calculated patterns is signified by the blue line.



Fig. S6 Crystal structures of  $Na_3SbS_4$  viewed along the (a) a-axis and (b) c-axis with the unit cell outlined. The Na, Sb, and S sites are represented by green, orange, and yellow balls, respectively.









(b)

Fig. S7 FE-SEM images of  $Na_3SbS_4$  prepared by (a) a liquid-phase technique with drying at 150 °C and (b) a mechanochemical technique.





#### Fig. S8 Raman spectrum of the precursor aqueous solution of $Na_2WS_4$ .





Fig. S9 XRD patters of  $Na_2WS_4$  prepared by a liquid-phase technique with drying at 150 °C,  $(NH_4)_2WS_4$ , and  $Na_2WS_4$  (JCPDS no. 00-041-1148).



Fig. S10 Amounts of  $H_2S$  gas as a function of time from  $Na_3SbS_4$  and  $Na_{2.88}Sb_{0.88}W_{0.12}S_4$  solid powders, normalised by sulfur in the samples. The humidity and room temperature during measurement were 68-74% and 23-25 °C, respectively.





Fig. S11 Nyquist plots at -25.3 and -25.9 °C of  $Na_{2.88}Sb_{0.88}W_{0.12}S_4$  before ( $\Box$ ) and after (O) an annealing process at 100 °C, respectively



Fig. S12 Current as a function of time of  $Na_{2.88}Sb_{0.88}Sb_{0.12}S_4$  green compact prepared by cold-pressing at 720 MPa and subsequent annealing at 100 °C. The measurement was conducted by a DC polarisation technique to estimate the electronic conductivity at 25 °C. The applied voltage was ca. 0.3 V.



Fig. S13 Meyer-Neldel plots for sulfide-based lithium-ion and sodium-ion conductors reported previously.<sup>17, 23, 26, 43</sup> The plots were prepared with reference to Ref. 23. The dash line indicates the conductivity threshold of 1 mS cm<sup>-1</sup>. The activation energy and the preexponential factor of  $Na_{2.88}Sb_{0.88}W_{0.12}S_4$  were 0.248 eV and 6.05 S cm<sup>-1</sup>, respectively.



Fig. S14 Crystal structure of  $Na_{2.88}Sb_{0.88}W_{0.12}S_4$  with the unit cell outlined. The Na, Sb, W, and S sites are represented by green, orange, grey, and yellow balls, respectively.

Table S1 Chemical composition of Na<sub>3</sub>SbS<sub>4</sub> prepared by a liquid-phase technique with drying at 150 °C. The values were determined by the RBS and ICP-AES measurements.

Analysis technique	Na / atomic%	Sb / atomic%	S / atomic%	Na / Sb	S / Sb
RBS	37.6	12.4	50.0	3.03	4.03
ICP-AES	75.0	25.0	N/A	3.01	N/A

\*RBS: Rutherford backscattering spectrometry, ICP-AES: Inductively coupled plasm atomic emission spectroscopy

#### Table S2 Crystallographic data for Na<sub>3</sub>SbS<sub>4</sub> prepared by a liquid-phase technique with drying at 150 °C.

Crystal systemTetragonalSpace group $P\overline{4}2_1c$ (no. 114)		onal (no. 114)	Lattice parameter Volume	$a = b = 7.1633(3)$ Å, $c = 7.2821(4)$ Å, $\alpha = \beta = \gamma = 90^{\circ}$ V = 373.665442 Å <sup>3</sup> , $Z = 2$		
Atom	Wyckoff site	g	X	y	Ζ.	U / Ų
Na1	4 <i>d</i>	1.0	0	1/2	0.4353(5)	0.0431
Na2	2 <i>b</i>	1.0	0	0	1/2	0.066
Sb	2a	1.0	0	0	0	0.0144
S	8 <i>e</i>	1.0	0.2995(4)	0.3268(4)	0.6842(3)	0.0232

 $*R_{wp} = 3.57, R_e = 1.71, R_P = 2.76, S = R_{wp}/R_e = 2.0882$ 

#### Table S3 Crystallographic data for $Na_{2.88}Sb_{0.88}W_{0.12}S_4$ prepared by a liquid-phase technique with heat treatment at 275 °C.

Crystal system	Tetragonal	Lattice parameter	$a = b = 7.1664(2)$ Å, $c = 7.257(3)$ Å, $\alpha = \beta = \gamma = 90^{\circ}$
Space group	$P\overline{4}2_1c$ (no. 114)	Volume	$V = 372.70 \text{ Å}^3, Z = 2$

X

Atom Wyckoff site

8

у



 $\mathcal{Z}$ 

U / Å $^2$ 

Na1	4 <i>d</i>	1.0	0	1/2	0.4394(7)	0.057
Na2	2b	0.88	0	0	1/2	0.05
Sb	2a	0.88	0	0	0	0.0171
W	2a	0.12	0	0	0	= U(Sb)
S	8 <i>e</i>	1.0	0.3031(5)	0.3263(5)	0.6855(3)	0.0245

 $*R_{wp} = 3.20, R_e = 1.73, R_P = 2.41, S = R_{wp}/R_e = 1.85$