

SUPPORTING INFORMATION

Unveiling the relationship between polymorphism and ionic conductivity in $\text{Na}_{3-x}\text{Sb}_{1-x}\text{W}_x\text{S}_4$ solid electrolyte for Na-ion batteries

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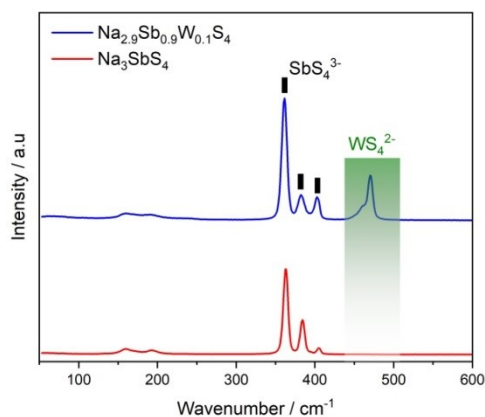


Figure S1 - Raman spectra of the prepared $\text{Na}_{3-x}\text{Sb}_{1-x}\text{W}_x\text{S}_4$ samples (nominal compositions $x=0$ and $x=0.1$).

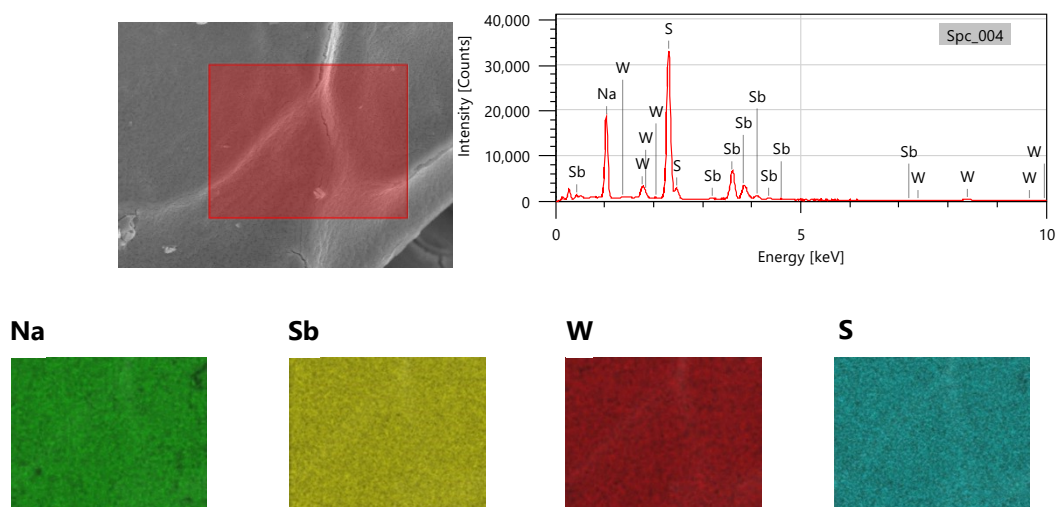


Figure S2 Example of SEM image and elemental mapping for the sample of nominal composition $\text{Na}_{2.9}\text{Sb}_{0.9}\text{W}_{0.1}\text{S}_4$.

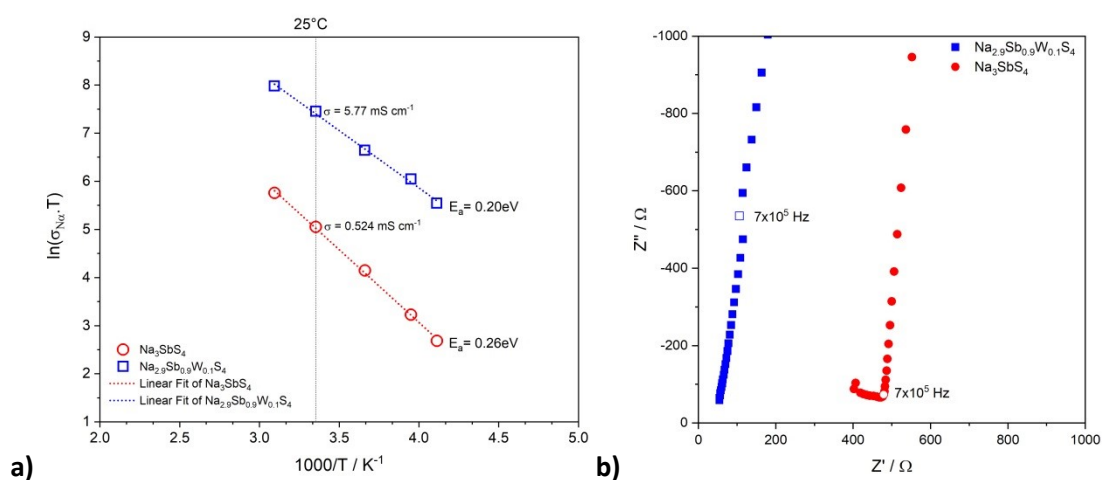


Figure S3 – Arrhenius plots of conductivity (a) and examples of Nyquist plots (b) for the two sample of nominal compositions Na_3SbS_4 and $Na_{2.9}Sb_{0.9}W_{0.1}S_4$

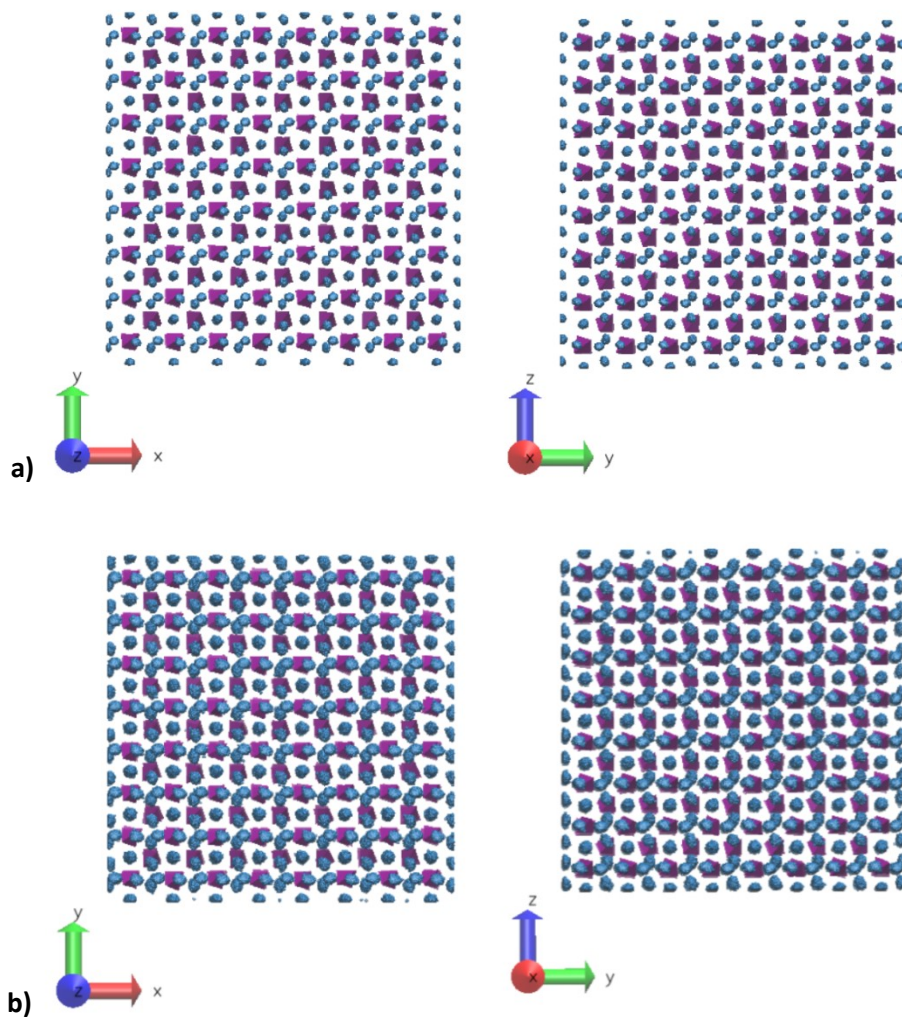


Figure S4 - Trajectory plots of Na ion in Na_3SbS_4 , as derived from MD simulations at 300K (a) and 700K (b). Purple polyhedra represent the coordination environment of Sb; blue dots represent the positions that the Na ions have occupied over the simulation time.

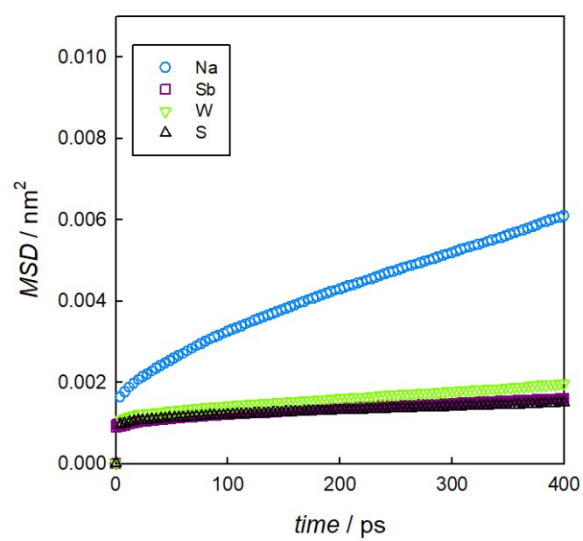


Figure S5 – Comparison of the ion MSD over simulation time for all the atomic species for the sample SbW12.5.

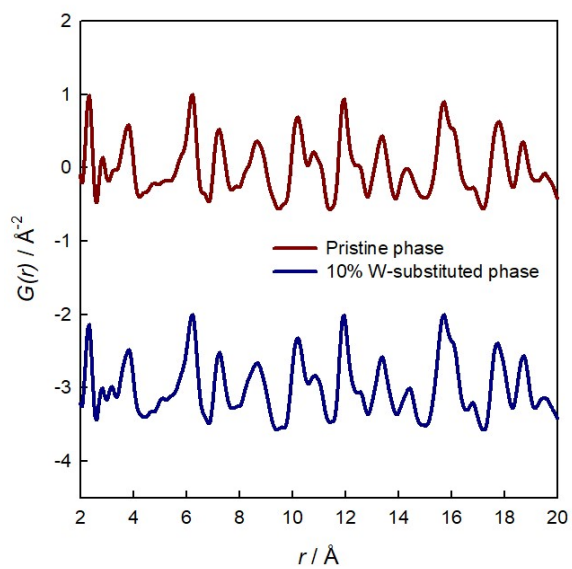


Figure S6 – Comparison between the PDF data of Na₃SbS₄ and Na_{2.9}Sb_{0.9}W_{0.10}S₄.

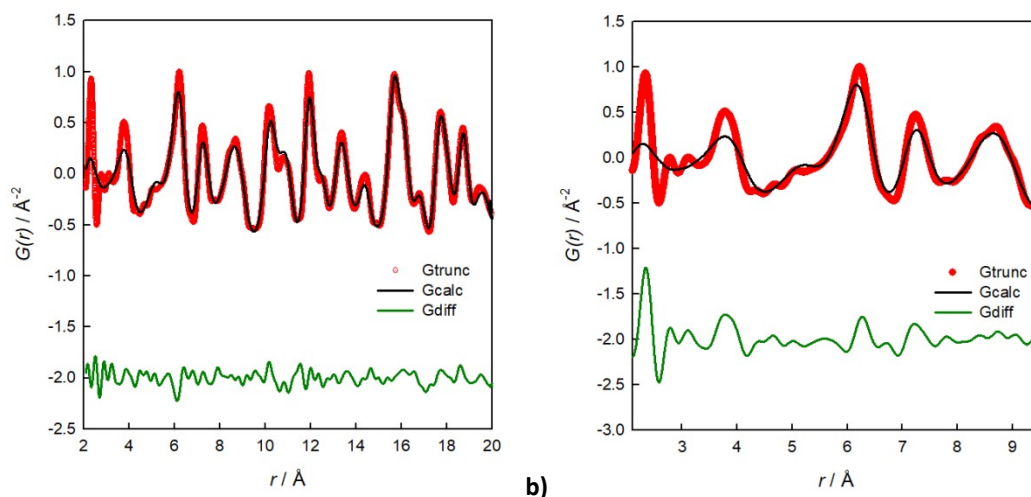


Figure S7 – Example of the difference between the experimental and the calculated PDFs based on the cubic model refined in the medium 20-50 Å r -range applied to two different r -ranges without further refinement, showing the low agreement between the experimental and computational models and the necessity to further refine the model: a) 2-20 Å ($R_{wp} = 38.14$); b) 2-9.50 Å ($R_{wp} = 45.66$)

Table S1 Potential model parameters and partial charges used for the description of the $\text{Na}_3\text{Sb}_1\text{S}_4$ (a) and $\text{Na}_{2.875}\text{Sb}_{0.875}\text{W}_{0.125}\text{S}_4$ (b) compositions. The pair potentials are in the form of the Buckingham two-body potentials ($U(r) = Ae^{-r/\rho} - Cr^{-6}$), where r is the interatomic distance.

Interaction	A	ρ	C
Na-S	1659.1800	0.3517	0.000
Sb-S	257.9196	0.5506	0.000
W-S	202.4500	0.5021	0.000
S-S	9387.0500	0.3550	1229.531

a)

atom	partial charge
Na	1.260550
Sb	3.005060
S	-1.6966773

b)

atom	partial charge
Na	1.260000
Sb	3.000000
W	2.540000
S	-1.64125

Table S2 – Room temperature Rietveld refined crystallographic parameters and agreement factors as derived from synchrotron data for a) Na_3SbS_4 and b) $\text{Na}_{2.9}\text{Sb}_{0.9}\text{W}_{0.1}\text{S}_4$.

a) Na_3SbS_4 (Space group: P -4 2_1 c). Phase content: 96.65%; NaSbS_2 (Space group: P -1) 3.35%.

R_Bragg = 3.58; Rwp: 9.51

$a = b$ (Å)	c (Å)	$\alpha=\beta=\gamma$ (°)	V (Å ³)
7.169052 (8)	7.294751 (11)	90	374.916 (1)

Species	x	y	z	Occupancy	B_{eq}
Sb	0	0	0	1	0.92 (1)
S	-0.2037 (14)	0.1716 (14)	-0.1824 (13)	1	1.37 (2)
Na1	0	1/2	0.4347 (28)	0.991 (4)	3.46 (5)
Na2	0	0	1/2	1	4.29 (6)

b) $\text{Na}_{2.9}\text{Sb}_{0.9}\text{W}_{0.1}\text{S}_4$ (Space group: I -4 3m). Phase content: 99.8%; WS_2 (Space group: P -1) 0.2%.

R_Bragg = 4.29; Rwp: 9.44

$a=b=c$ (Å)	$\alpha=\beta=\gamma$ (°)	V (Å ³)
7.208060 (11)	90	374.503 (2)

Species	x	y	z	Occupancy	B_{eq}
Sb	0	0	0	0.90 (1)	1.21 (2)
W	0	0	0	0.10 (1)	1.21 (2)
S	0.18551 (9)	0.18551 (9)	0.18551 (9)	1	2.43 (3)
Na1	0	0.0571 (6)	1/2	0.236 (1)	2.59 (14)