Supporting Information for: $Na_{11}Sn_2PS_{12}$: A New Solid State Sodium Superionic Conductor

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Table S1: Crystallographic data for $Na_{11}Sn_2PS_{12}$ obtained from single crystal X-ray diffraction.

Crystal data	
Formula	$Na_{10.78}Sn_2PS_{12}$
Formula Weight	900.99
Crystal System	tetragonal
Space group	$I4_1/acd$:2 (No.142)
a, b, c (Å)	13.6148(3), 13.6148(3), 27.2244(7)
V (Å^3)	5046.4(3)
Z	8
Calc. density (g/cm^3)	2.373
Abs. coef. μ (MoKa) (/mm)	3.213
F(000)	3407
Crystal Size (mm)	0.02 ×0.02× 0.07
Data Collection	
Temperature (K)	280
Radiation (Å)	Mo-Kα 0.71073
Theta range for data collection	1.5, 30.0
Index ranges	$-18 \le h \le 19$; $-19 \le k \le 18$; $-36 \le l \le 29$
Reflections collected	14755
Independent reflections	1820 (R_{int} = 0.0382)
Completeness to θ = 25.242°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.6468
Refinement	
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1820 / 0 / 71
Goodness-of-fit on F^2	1.357
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.0936
R indices (all data)	R1 = 0.0543, wR2 = 0.0992
Extinction coefficient	n/a
Largest diff. peak and hole	2.107 and -0.762 e.Å^{-3}

Table S2: Bond distances in $Na_{11}Sn_2PS_{12}$ obtained from single crystal X-ray diffraction data.

Atom1	Atom2	Bond Distance (Å)
Sn1	S1	2.3793(12) Å, ×2
Sn1	S2	2.3794(12) Å, ×2
P1	S3	2.040(2) Å, ×4
Na1 Na1	S1 S1	2.967(4) Å 3.293(5) Å
Na1 Na1	S2 S2	2.893(4) Å 3.190(4) Å
Na1 Na1	S3 S3	2.967(6) Å 3.003(6) Å
Na2	S1	2.893(3) Å, ×2
Na2	S2	3.352(3) Å, ×2
Na2	S3	2.942(6) Å, ×2
Na3	S1	2.830(5) Å, ×2
Na3	S2	2.803(5) Å, ×2
Na3	S3	3.289(3) Å, ×2
Na4	S1	2.9675(13) Å, ×2
Na4	S2	2.6928(12) Å, ×2
Na4	S3	3.332(3) Å, ×2
Na5	S1	2.827(3) Å, ×2
Na5	S2	2.785(3) Å, ×2
Na5	S3	3.362(5) Å, ×2
Na1	Na3	3.413(3) Å, ×2
Na1	Na4	3.420(3) Å, ×2
Na1	Na5	3.453(6) Å, 3.380(6) Å
Na2	Na3	3.4259(7) Å, ×2
Na2	Na4	3.4092(4) Å, ×2

Table S3: Anisotropic displacement parameters of $Na_{11}Sn_2PS_{12}$ obtained from single crystal X-ray diffraction at 280K.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Sn1	0.0214(3)	0.0200(3)	0.0245(2)	-0.0008(2)	0	0
S1	0.0276(7)	0.0263(7)	0.0302(7)	-0.0004(5)	0.0042(5)	-0.0030(5)
S2	0.0233(6)	0.0280(7)	0.0271(6)	0.0009(5)	0.0025(4)	0.0010(5)
S3	0.0453(9)	0.0460(9)	0.0508(10)	-0.0128(7)	0.0110(7)	0.0058(8)
P1	0.0221(12)	0.0221(12)	0.0285(14)	0	0	0
Na1	0.085(4)	0.057(3)	0.077(3)	-0.003(2)	0.042(2)	-0.008(2)
Na2	0.062(5)	0.143(8)	0.041(4)	0	0	-0.061(5)
Na3	0.020(2)	0.131(6)	0.127(5)	0.092(4)	0	0
Na4	0.025(3)	0.294(14)	0.167(8)	-0.160(8)	-0.007(3)	-0.001(4)
Na5	0.192(8)	0.192(8)	0.024(3)	-0.009(3)	0.009(3)	-0.143(8)

Table S4. Parameters of the fit for the impedance data of $Na_{11}Sn_2PS_{12}$ at -20°C.

Element	**Value**
R1	66.1 Ω
R2	725.6 Ω
CPE1-T	1.186E-8 F
CPE1-P	0.76458
CPE2-T	5.624E-6 F
CPE2-P	0.8012
W1-R	250.9 Ω
W1-T	0.01096
W1-P	0.42701

Table S5. Calculated diffusion coefficients along the *a*, *b*, and *c* axes, from 600 K to 1050K.

Simulated temperature	along *a* axis ($cm^2\ s^{-1}$)	along *b* axis ($cm^2\ s^{-1}$)	along *c* axis ($cm^2\ s^{-1}$)
750K	5.3×10^{-6}	6.3×10^{-6}	6.6×10^{-6}
900K	1.1×10^{-5}	1.5×10^{-5}	0.9×10^{-5}
1050K	2.5×10^{-5}	1.8×10^{-5}	1.6×10^{-5}

Table S6. Bottleneck size for Na^+ ion transport derived from the single crystal structure

Na^+-Na^+	Bottleneck size (Å)
Na1-Na3	2.47 Å
Na1-Na4	2.48 Å
Na1-Na5	2.45 Å, 2.53 Å
Na2-Na3	2.47 Å
Na2-Na4	2.51 Å

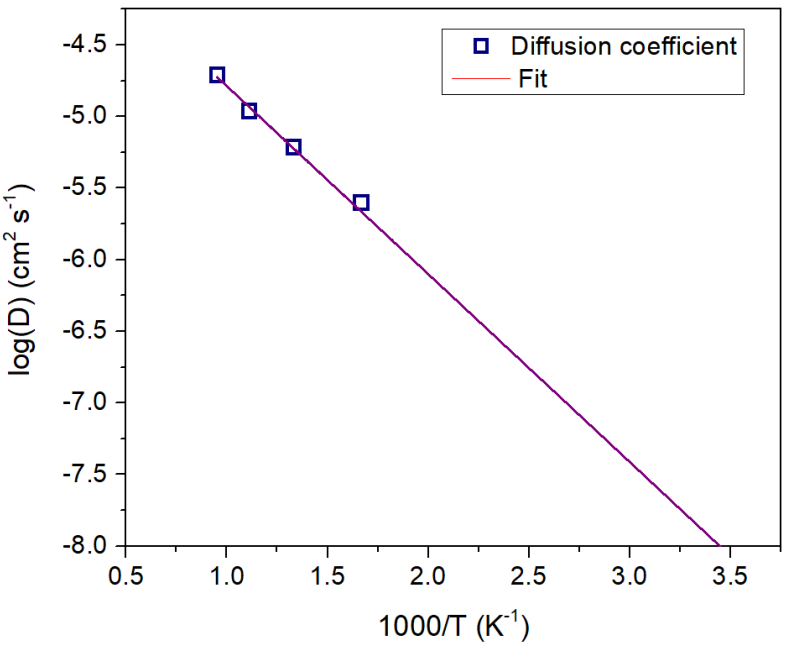

Figure S1. Calculated Na^+ ion diffusivity in $Na_{11}Sn_2PS_{12}$ from AIMD simulations, and the Arrhenius fit to the data used to determine the extrapolated diffusion coefficient at 300K of 2.2×10^{-8} cm^2 s^{-1}.

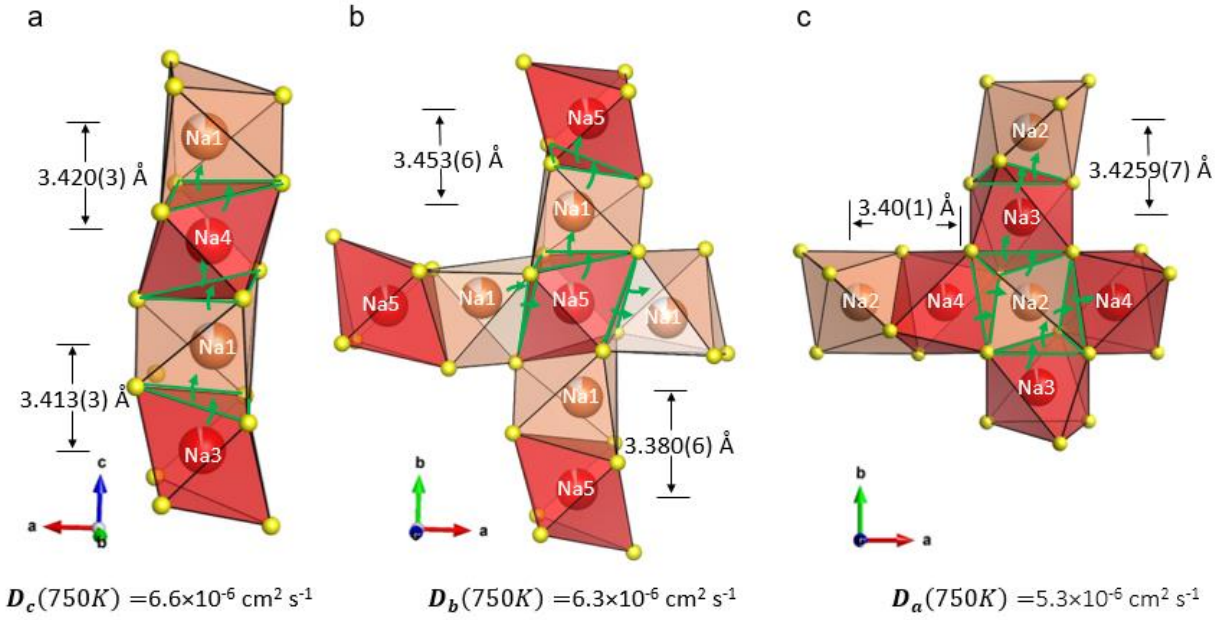

Figure S2. Na^+-Na^+ atomic distances and calculated diffusion coefficients at 750K ; (a) along the *c* axis, (b) along the *b* axis and (c) along the *a* axis.