Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information

Design of sodium superionic conductors based on multiple crystal structure prediction methods

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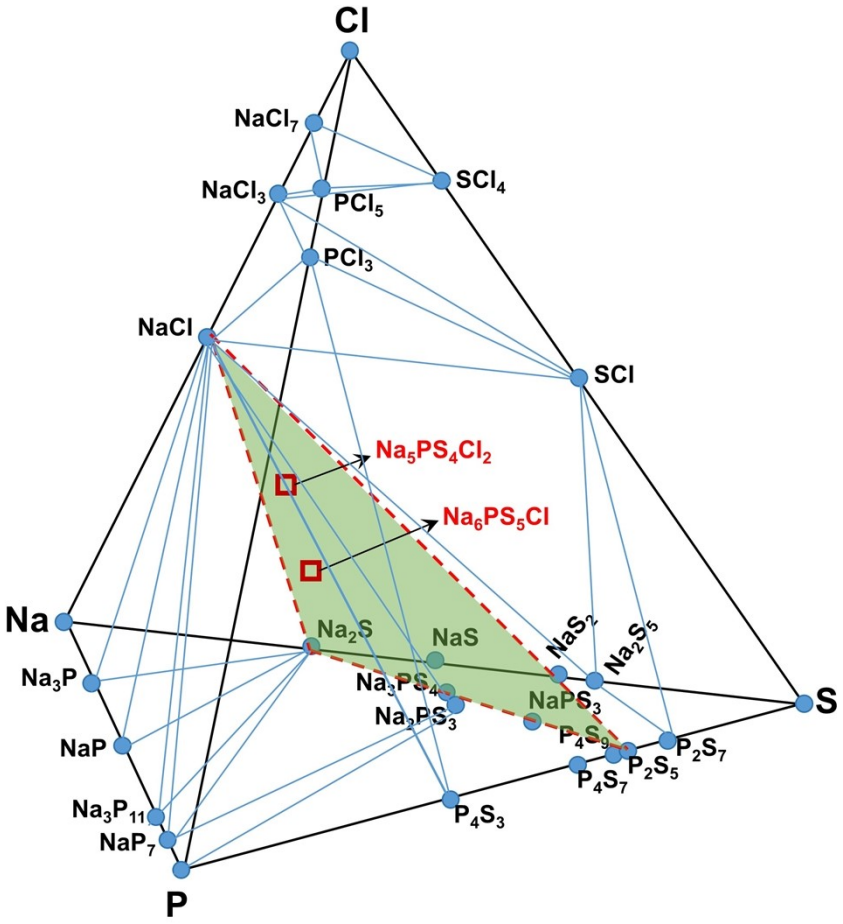

Fig. S1 Na-P-S-Cl Four-Component Phase Diagram.

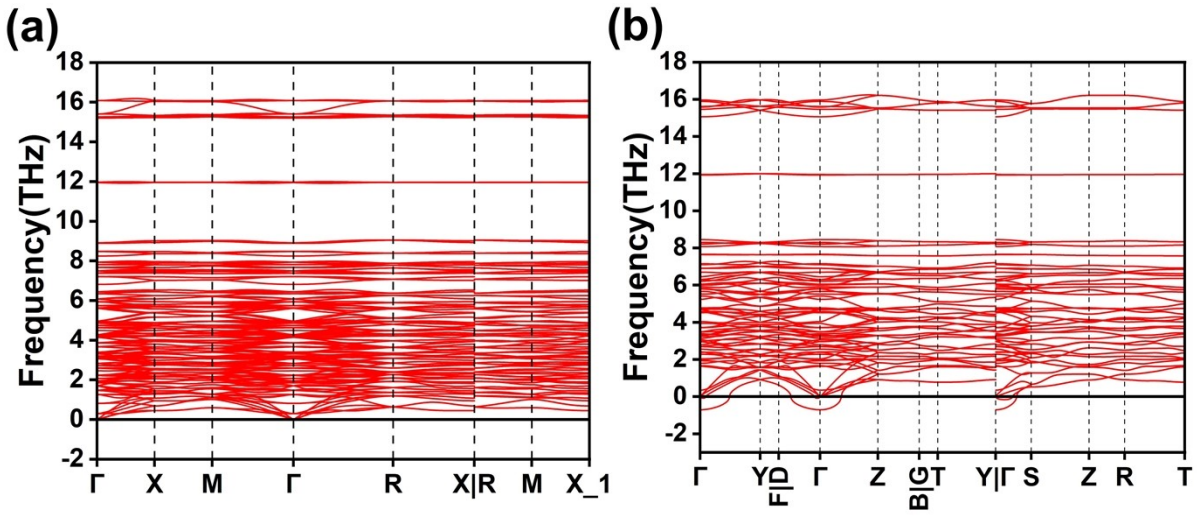

Fig. S2 The phonon spectra of (a) NPSC1, and (b) NPSC2.

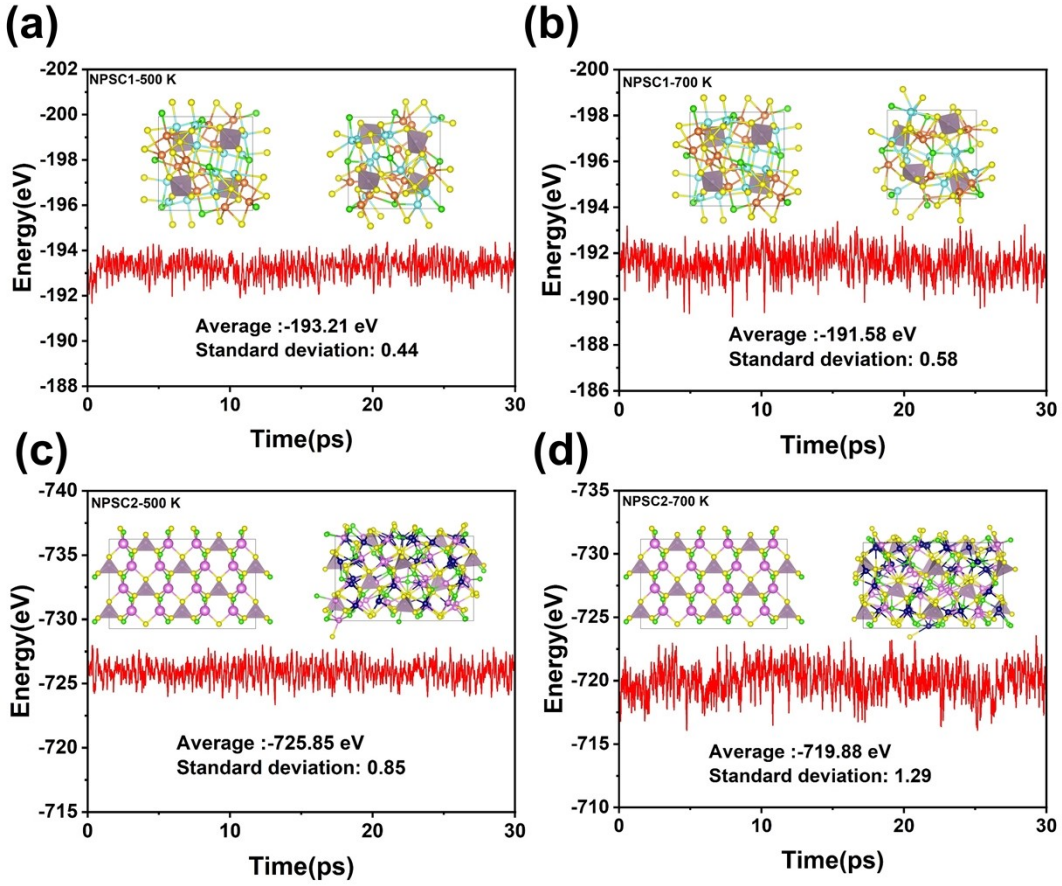

Fig. S3 Total energy fluctuation during the AIMD simulations at 500 K and 700 K of (a) NPSC1, and (b) NPSC2.

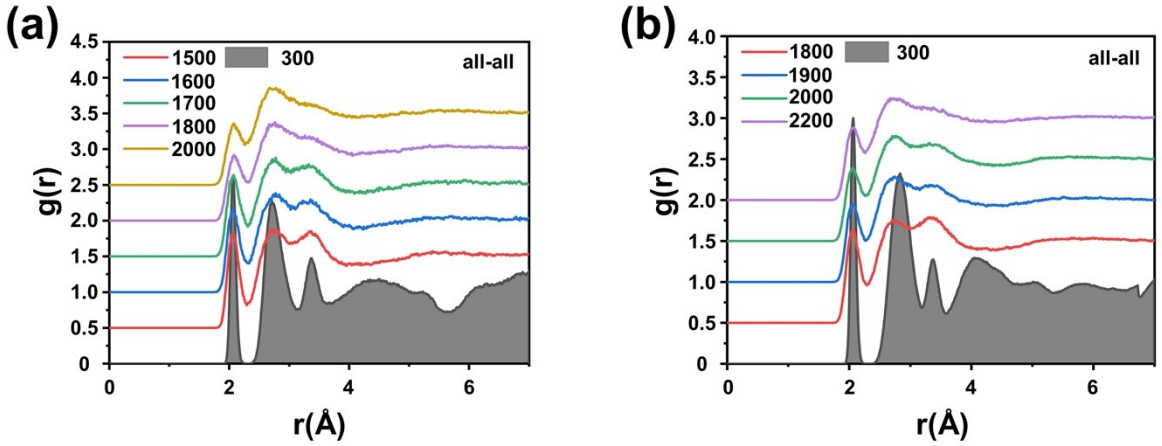

Fig. S4 The radial distribution function of all-all in (a) NPSC1, and (b) NPSC2

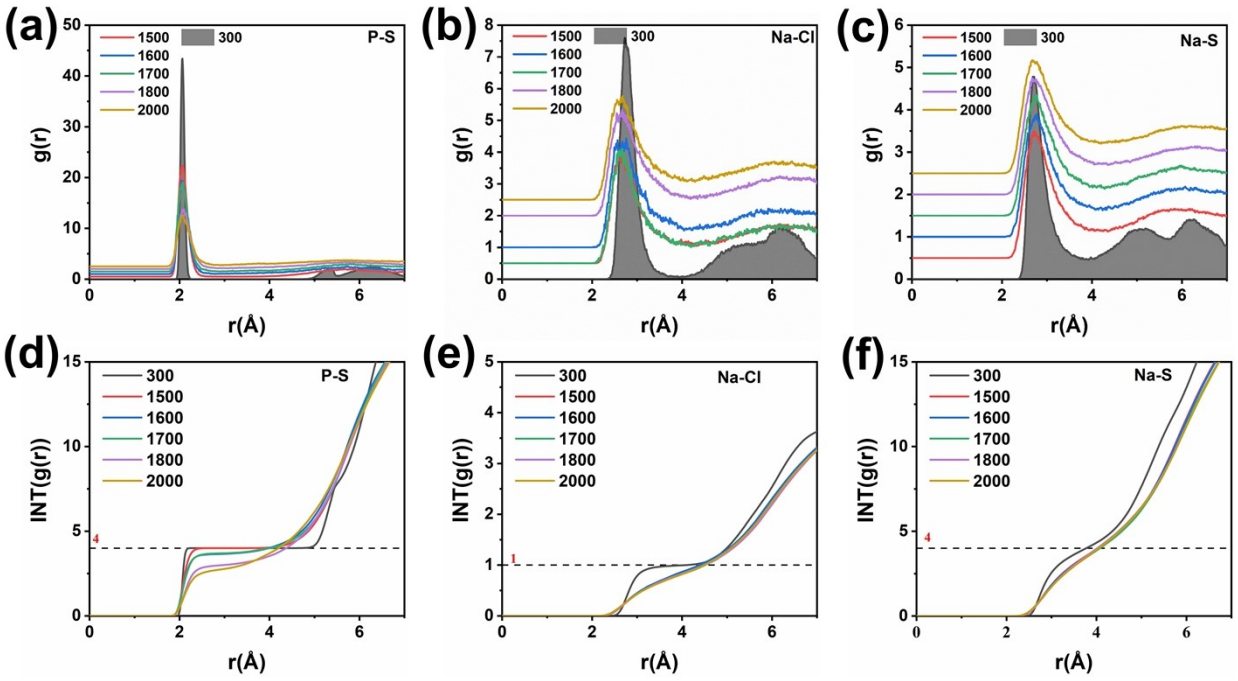

Fig S5 (a-c) The radial distribution function of P-S, Na-Cl, and Na-S in NPSC1. (d-f) The integral of the radial distribution function of P-S, Na-Cl, and Na-S in NPSC1.

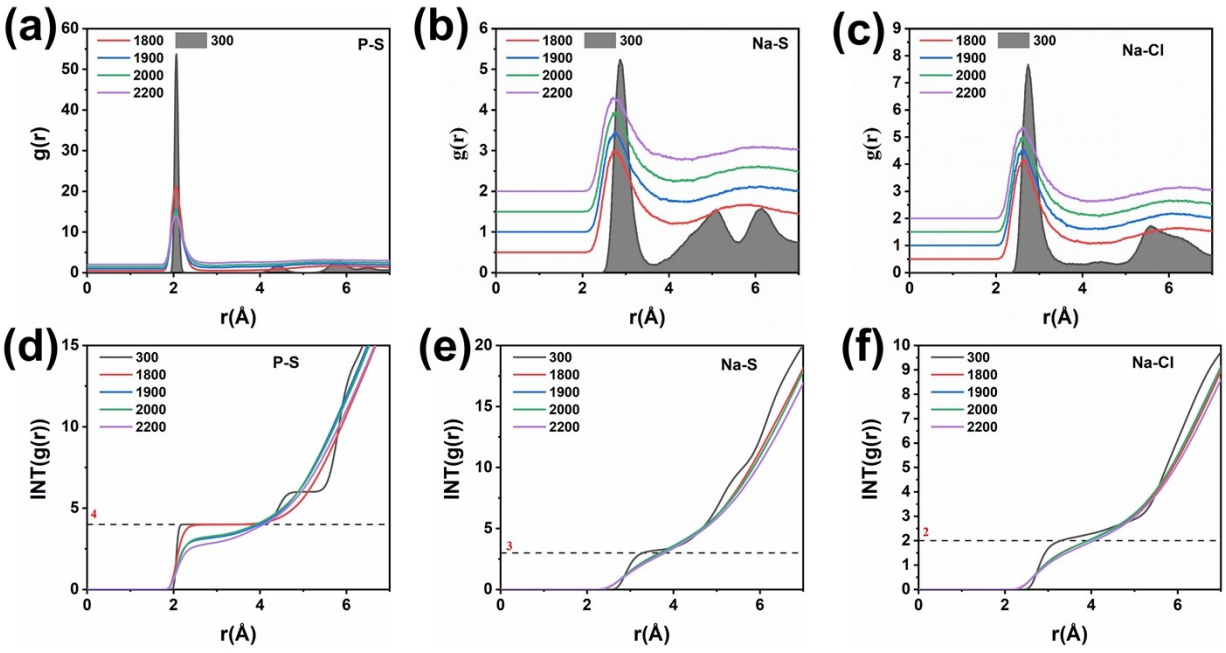

Fig S6 (a-c) The radial distribution function of P-S, Na-Cl, and Na-S in NPSC2. (d-f) The integral of the radial distribution function of P-S, Na-Cl, and Na-S in NPSC2.

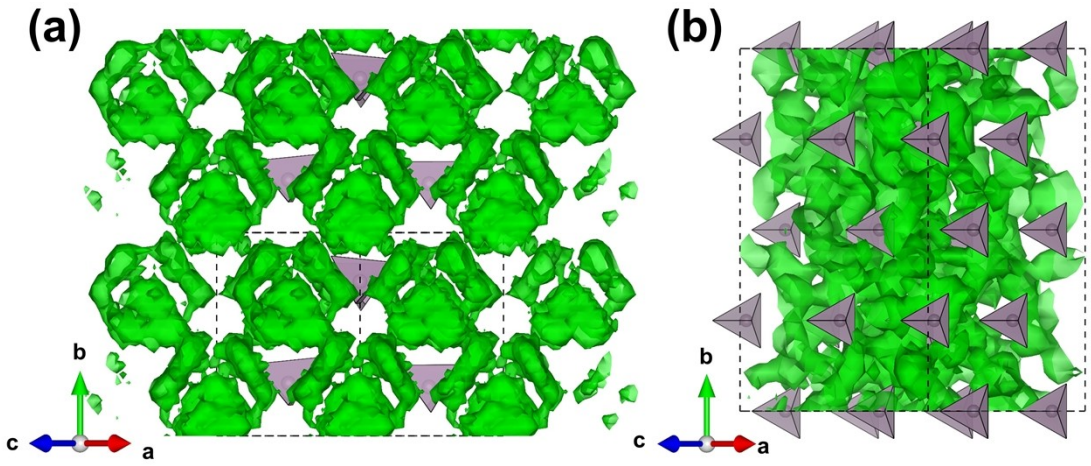

Fig. S7 The Na-ions probability density superimposed (green) on the anion sublattice of NPSC1 (1000 K) and NPSC2 (1300 K), the data from AIMD simulations.

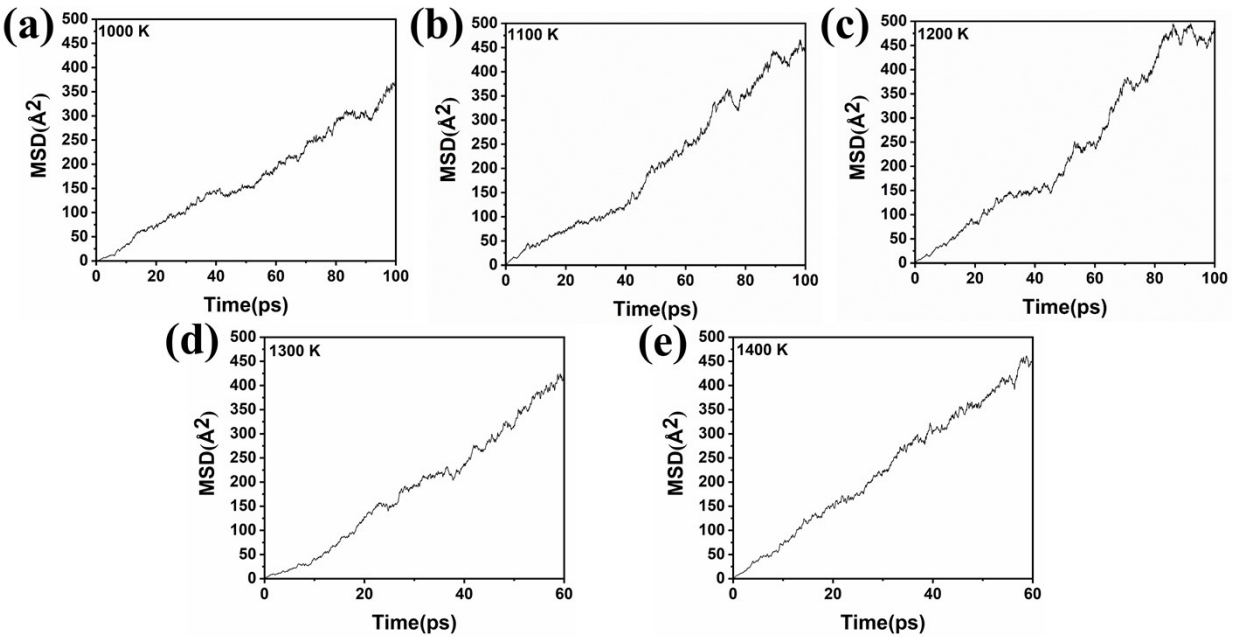

Fig. S8 MSD plots of NPSC1 for AIMD simulations. (a) 100ps AIMD simulation at 1000K. (b) 100ps AIMD simulation at 1100K. (c) 100ps AIMD simulation at 1200K. (d) 60ps AIMD simulation at 1300K. (e) 60ps AIMD simulation at 1400K.

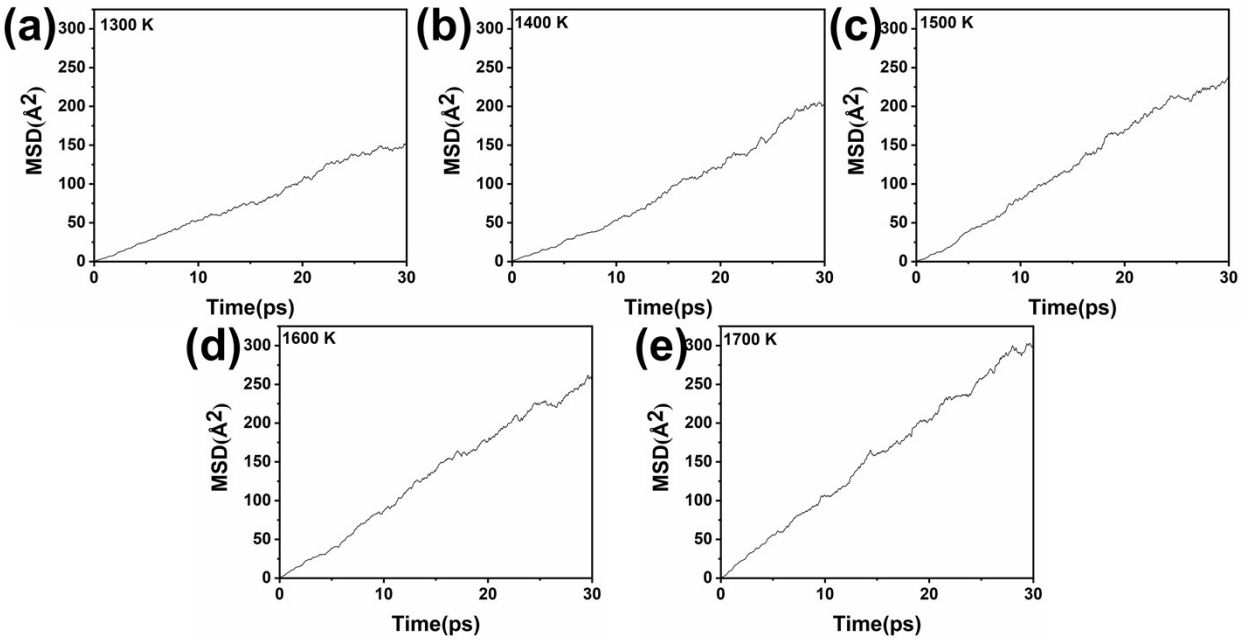

Fig. S9 MSD plots of NPSC2 for AIMD simulations. (a) 30ps AIMD simulation at 1300K. (b) 30ps AIMD simulation at 1400K. (c) 30ps AIMD simulation at 1500K. (d) 30ps AIMD simulation at 1600K. (e) 30ps AIMD simulation at 1700K

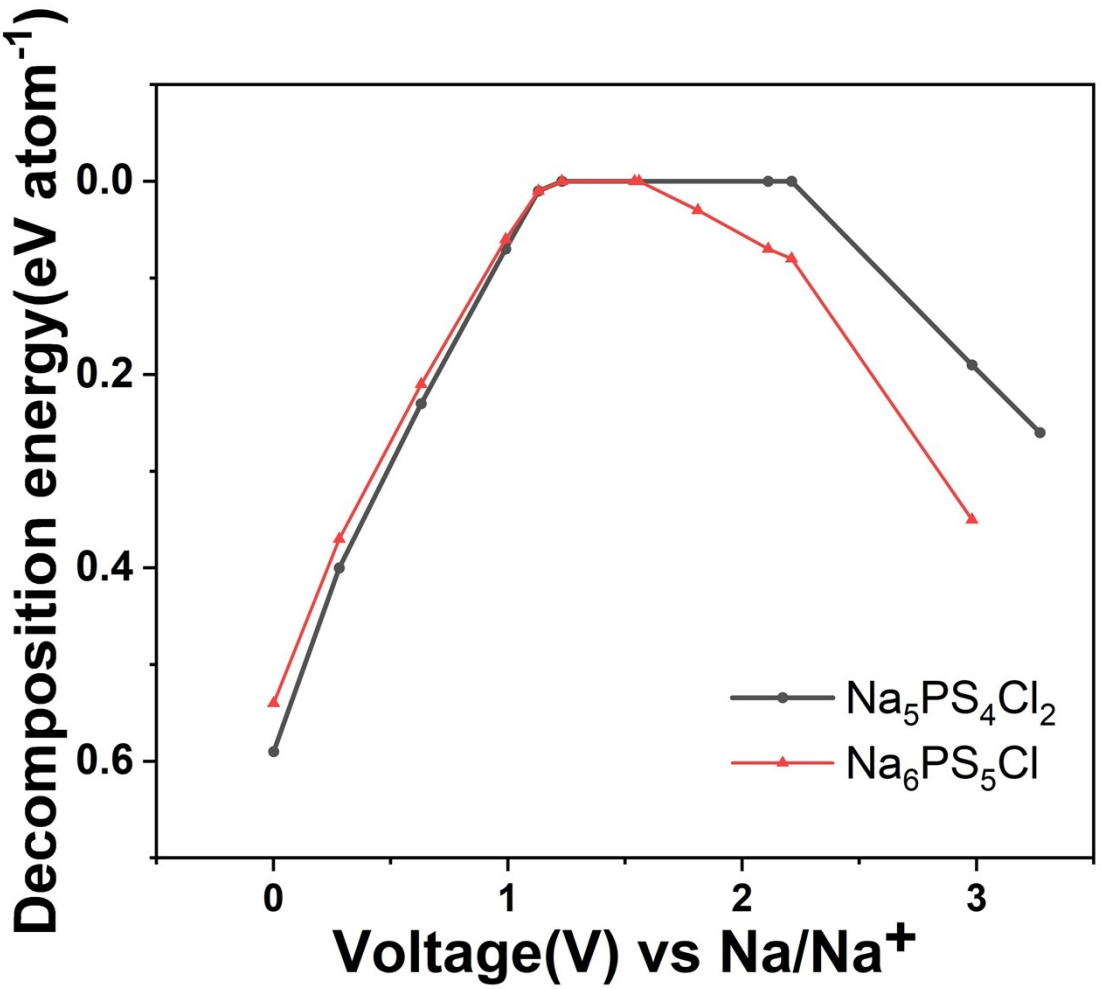

Fig. S10 The decomposition energy of NPSC1 and NPSC2as a function of the chemical potential of Na-ions.

Table S1. Structure parameters of Na_6PS_5Cl.

Space group: $P2_13$

a = b = c = 10.8677 Å.

Atom	Wyckoff position	Atomic coordinates		
		x	y	z
Na1	12b	0.59261	0.19284	0.89028
Na13	12b	0.03536	0.59030	0.70574
P1	4a	0.75939	0.75939	0.75939
S1	12b	0.64670	0.34774	0.38442
S13	4a	0.27138	0.27138	0.27138
S17	4a	0.65069	0.65069	0.65069
Cl1	4a	0.03684	0.03684	0.03684

Table S2. Structure parameters of $Na_5PS_4Cl_2$.

Space group: *Amm2*

a = 8.0638 Å, b = 10.9395 Å, c = 6.7199 Å.

Atom	Wyckoff position	Atomic coordinates		
		x	y	z
Na1	8f	0.75922	0.30659	0.40075
Na9	2b	0.50000	0.00000	0.38679
P1	2a	0.00000	0.00000	0.42183
S1	4d	0.00000	0.84850	0.23791
S5	4c	0.79327	0.00000	0.60281
Cl1	4e	0.50000	0.69684	0.65657

Table S3. The percolation radius of NPSC1 and NPSC2, and the phonon band center.

Solid electrolyte	percolation radius (p_r)	phonon band center (THz)
NPSC1	0.95 Å	5.36 THz
NPSC2	0.65 Å	5.25 THz

Table S4. Reduction and oxidation reactions of NPSC1 and NPSC2 as a function of the chemical potential of Na-ions.

Solid electrolyte	Potential (V)	E_D (eV/atom)	Phase equilibria
NPSC1	0.00	0.54	Na_3P,Na_2S,NaCl
	0.28	0.37	NaP,Na_2S,NaCl
	0.63	0.21	Na_3P_{11},Na_2S,NaCl
	0.99	0.06	NaP_7,Na_2S,NaCl
	1.13	0.01	Na_2PS_3,Na_2S,NaCl
	1.23	0.00	NPSC1
	1.54	0.00	NaS,Na_3PS_4,NaCl
	1.56	0.00	NaS_2,Na_3PS_4,NaCl
	1.81	0.03	Na_3PS_4,Na_2S_5,NaCl
	2.11	0.07	Na_2PS_3,Na_2S_5,NaCl
	2.21	0.08	P_2S_7,Na_2S_5,NaCl
	2.98	0.35	P_2S_7,S,NaCl
NPSC2	0.00	0.59	Na_3P,Na_2S,NaCl
	0.28	0.40	NaP,Na_2S,NaCl
	0.63	0.23	Na_3P_{11},Na_2S,NaCl
	0.99	0.07	NaP_7,Na_2S,NaCl
	1.13	0.01	Na_2PS_3,Na_2S,NaCl
	1.23	0.00	NPSC2
	2.11	0.00	Na_2S_5,Na_2PS_3,NaCl
	2.21	0.00	Na_2S_5,P_2S_7,NaCl
	2.98	0.19	S, P_2S_7,NaCl
	3.27	0.26	NaCl,P_2S_7,SCl