Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION for:

A Novel Phase of Superionic Conductor β'-Na_3PS_4 with Large Band Gap and Low Migration barrier

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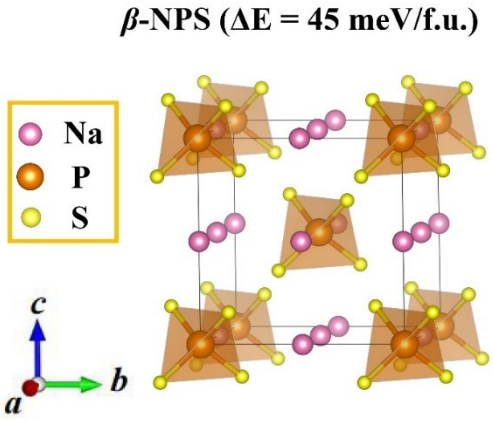

Fig. S1 Crystal structures of β-NPS. The ΔE is defined to be E(β-NPS) - E(α-NPS).

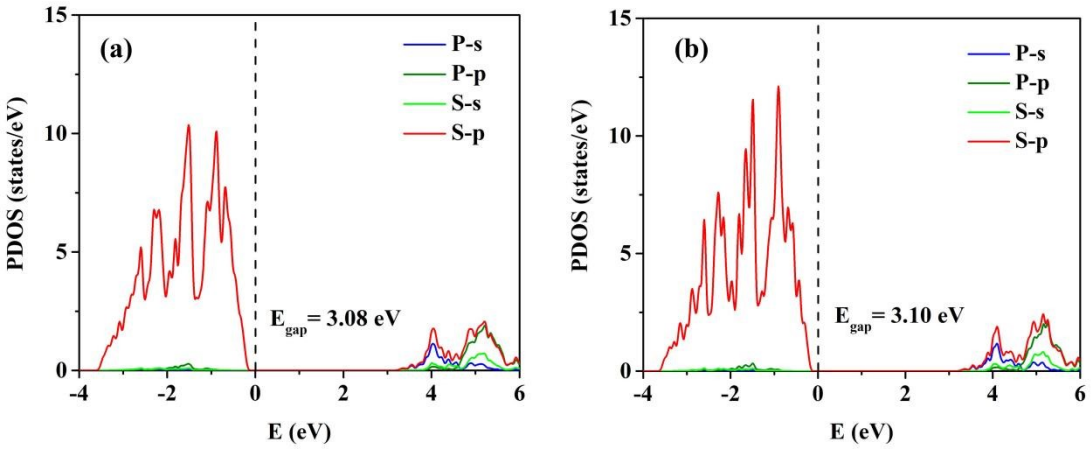

Fig. S2 Projected density of states of the (a) α-NPS and (b) β-NPS.

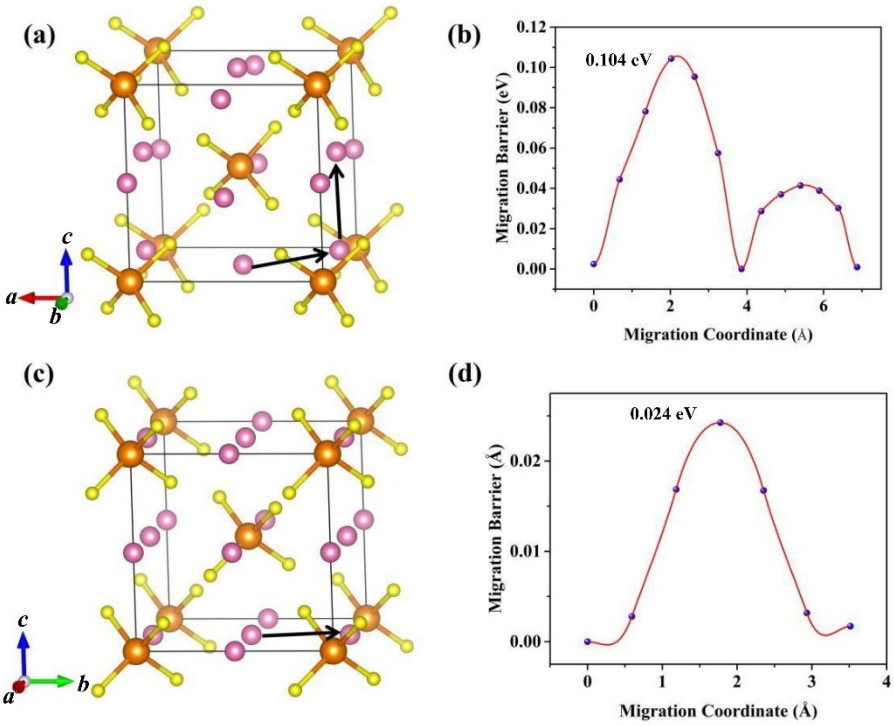

Fig. S3 Na ions migration channels in (a) α-NPS and (c) β-NPS. Migration barriers of Na ions in (b) α-NPS and (d) β-NPS.

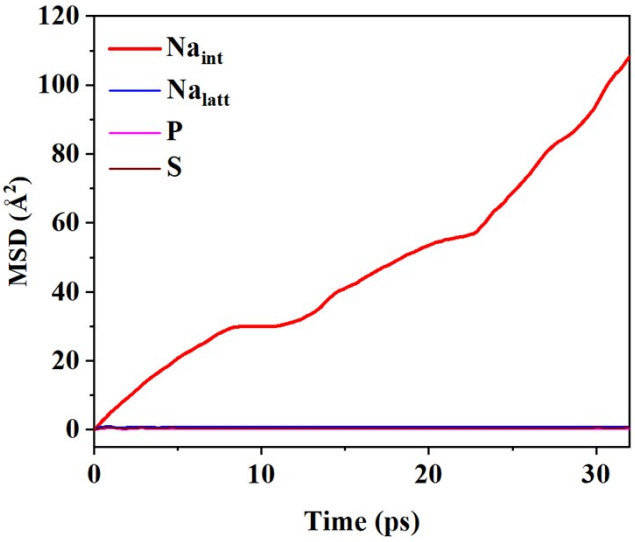

Fig. S4 The MSD of interstitial Na, lattice Na, P and S atoms in *β*′-NPS simulated at 500 K for 32 ps.

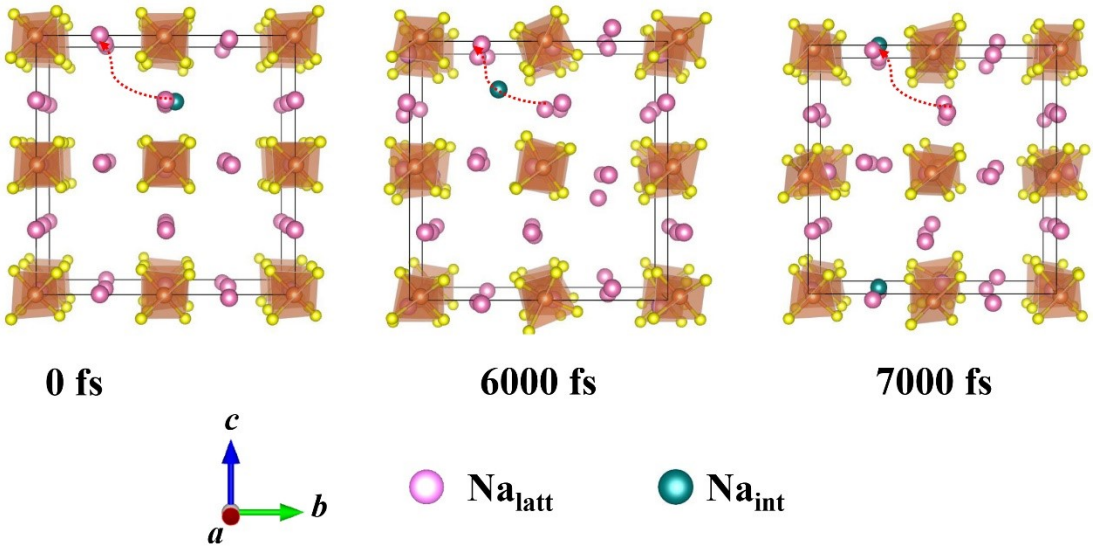

Fig. S5 Snapshots for the migration of interstitial Na in the *β*′-NPS at 500 K for 7000 fs. The red arrows on snapshots show Na-ion migration direction.

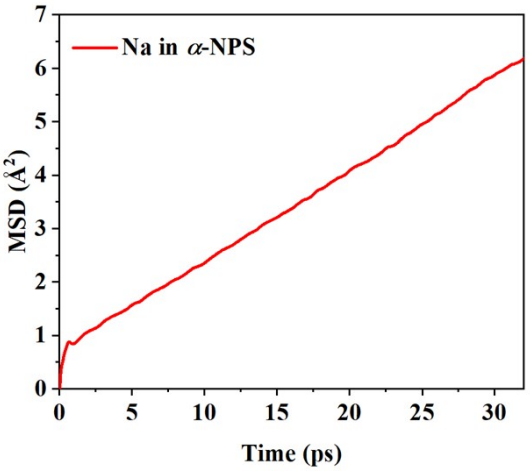

Fig. S6 MSD of per one Na atom in α-NPS simulated at 500 K for 32 ps.

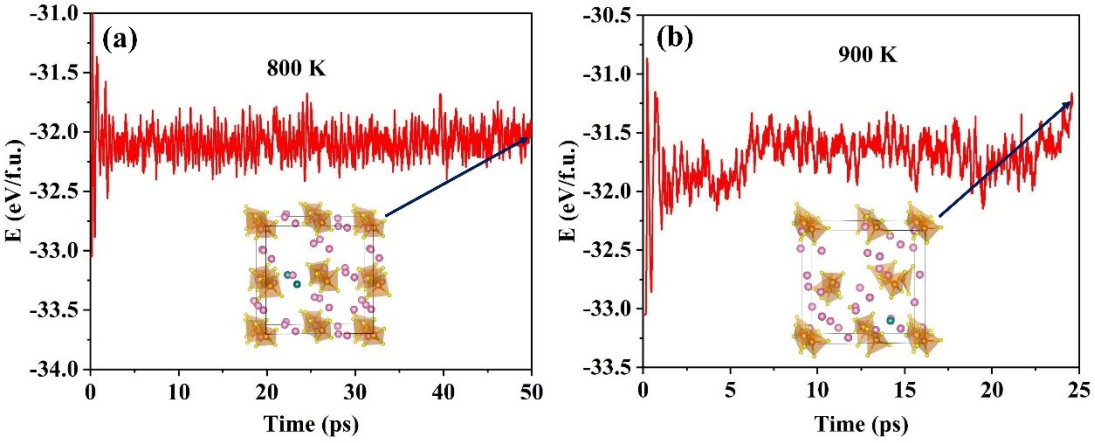

Fig. S7 The evolutions of the potential energy of β'-NPS during AIMD simulations at (a) 800 K and (b) 900 K. The insets are final configuration of β'-NPS supercell obtained from AIMD simulations.

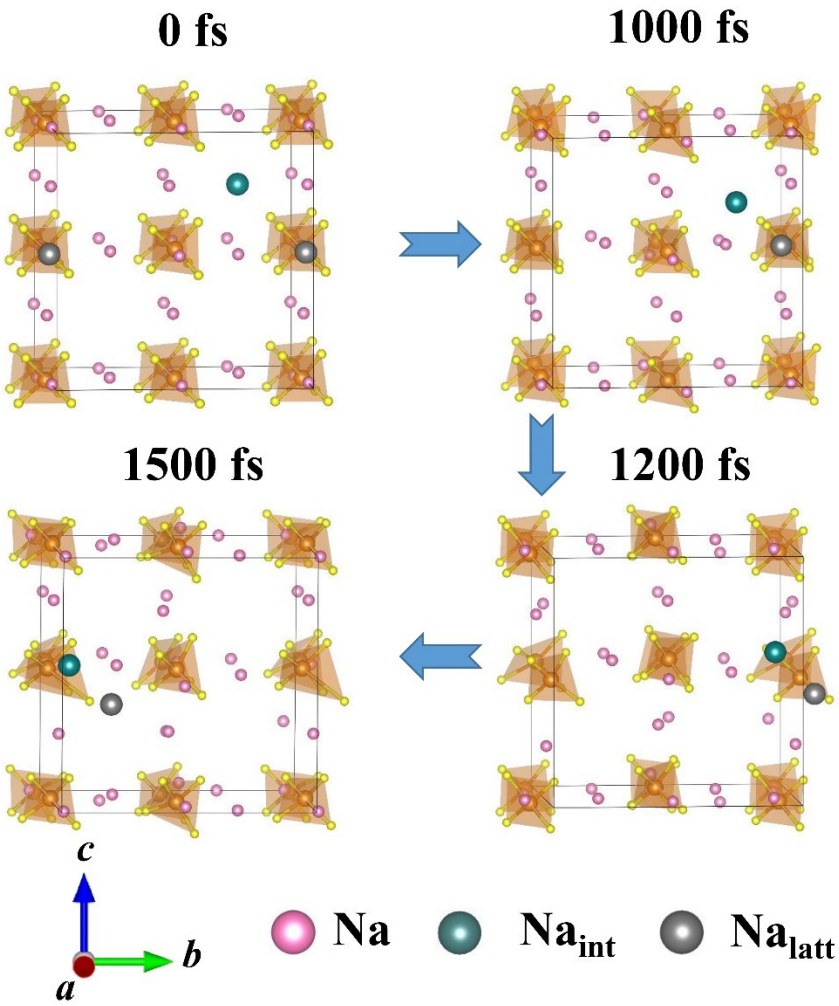

Fig. S8 Snapshots for the kick-off migration of Na in the β'-NPS at 800 K for 1500 fs.

Table S1. Lattice constants of β'-, α- and β-phases of NPS.

	Crystal system	Space group		a(Å)	c(Å)
β'-NPS	cubic	$P\bar{4}3m$		6.802	6.802
α-NPS	tetragonal	$P4\bar{2}_1c$	Cal.	6.982	7.116
			Exp.	6.962[a]	7.092 [a]

β-NPS	cubic	$I\bar{4}3m$	Cal.	7.012	7.012
			Exp.	6.989[b]	6.989[b]

[a]Data come from Ref.1

[b]Data come from Ref.2

Table S2. Average bond lengths of Na-S and P-S in the NaS_4 and PS_4 tetrahedra of the NPS polymorphs.

	α-NPS	β'-NPS	β-NPS
$d_{\text{Na-S}}$ (Å)	2.913	2.779	2.863
$d_{\text{P-S}}$ (Å)	2.067	2.068	2.070

Table S3. Calculated elastic constants (in GPa), Bulk modulus (*B*, in GPa), Young's modulus (*E*, in GPa), Shear modulus (*G*, in GPa) and *B/G* of β'-NPS and sodium metal[3].

	β'-NPS	Na
C_{11}	22.4	9.8
C_{12}	3.3	7.9
C_{44}	2.0	6.6
B	9.7	8.5
E	10.5	8.5
G	4.0	3.2
B/G	2.43	2.66

Table S4. Calculated phase equilibria for β'-NPS.

Voltage range vs Na^+/Na (V)	Δn_{Na} per formula	Phase equilibria
0–0.62	8	Na_3P, Na_2S
0.62–0.81	6	NaP, Na_2S
0.81–1.17	5	P, Na_2S

1.17–1.31	1	Na_2PS_3, Na_2S
1.31–1.98	0	Na_3PS_4
1.98–2.25	-1	Na_2PS_3, S
2.25-2.93	-2	$NaPS_3$, S
>2.93	-3	P, S

Reference

1. T. Famprikis, H. Bouyanfif, P. Canepa, M. Zbiri, J. A. Dawson, E. Suard, F. Fauth, H. Y. Playford, D. Dambournet, O. J. Borkiewicz, M. Courty, O. Clemens, J.-N. Chotard, J.-N. M. S. Islam and C. Masquelier, *Chem. Mater.,* 2021, **33**, 5652-5667.
2. M. Jansen and U. Henseler, *J. Solid State Chem.,* 1992, **99**, 110-119.
3. S. L. Shang, A. Saengdeejing, Z. G. Mei, D. E. Kim, H. Zhang, S. Ganeshan, Y. Wang, Z. K. Liu, *Comput. Mater. Sci.,* 2010, **48**, 813-826.