Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information for

Crystal Structure of High-temperature Polymorph β-Na_3PS_4

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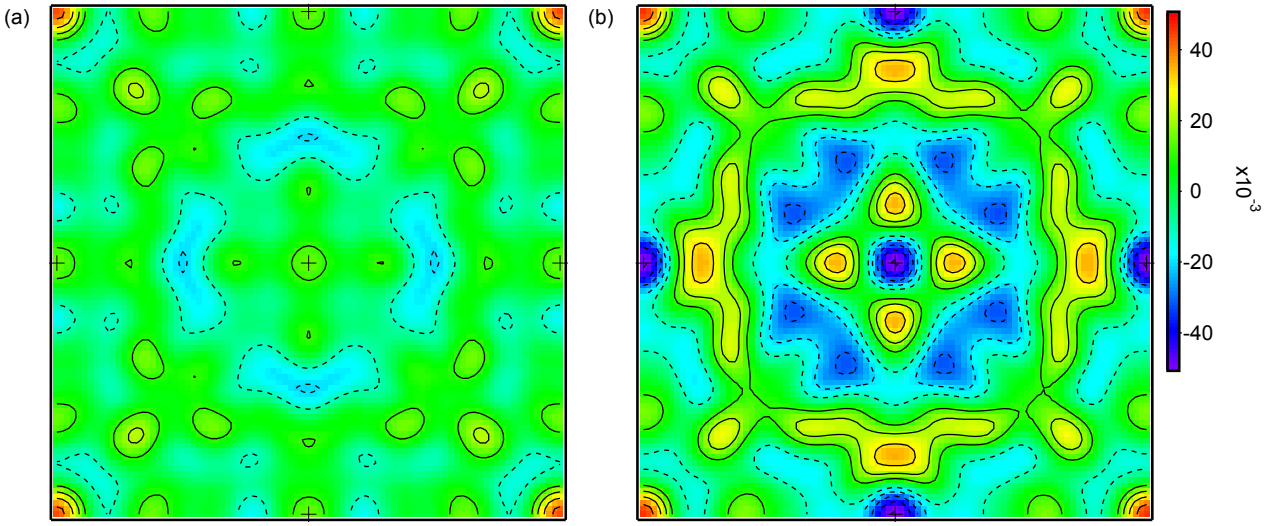

Figure S1 Difference Fourier map at (100) plane (x = 0) for β-Na_3PS_4 at 600 K with (a) and without (b) the site splitting of Na. The contour level spacing is 0.01 Å^{-3}. Solid and broken lines represent positive and negative values respectively, while zero contours are not drawn. The average sodium positions (6*b*) are plotted as crosses.

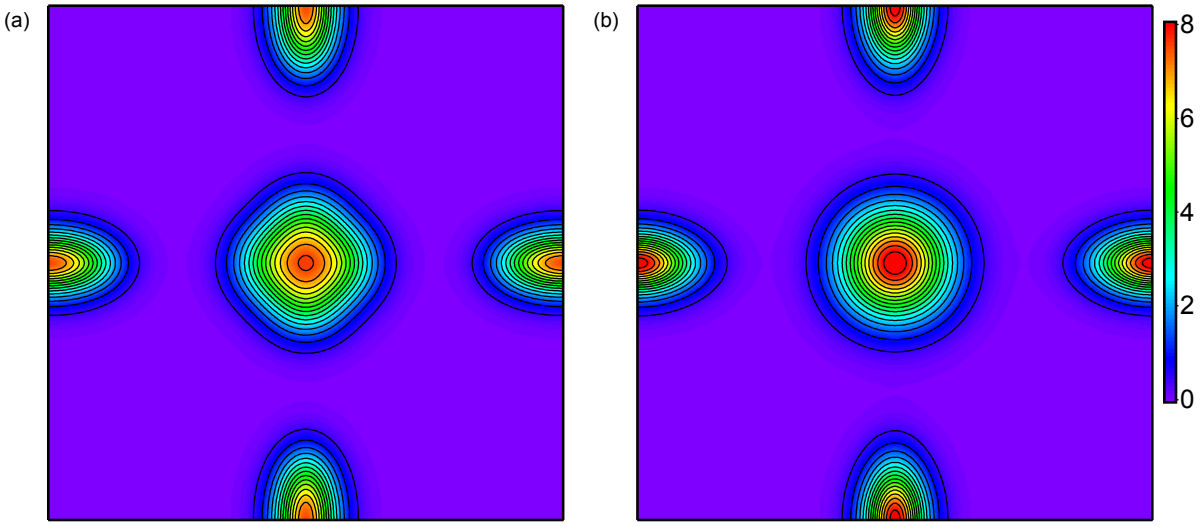

Figure S2 Electron density distribution at (001) plane (x = 0) about Na sites calculated from refined structural parameters of β-Na_3PS_4 at 600 K with (a) and without (b) the site splitting. The contours are drawn up to 8 Å^{-3} with intervals of 0.5 Å^{-3}. Electron density from phosphorus and sulphur are omitted for clarity.

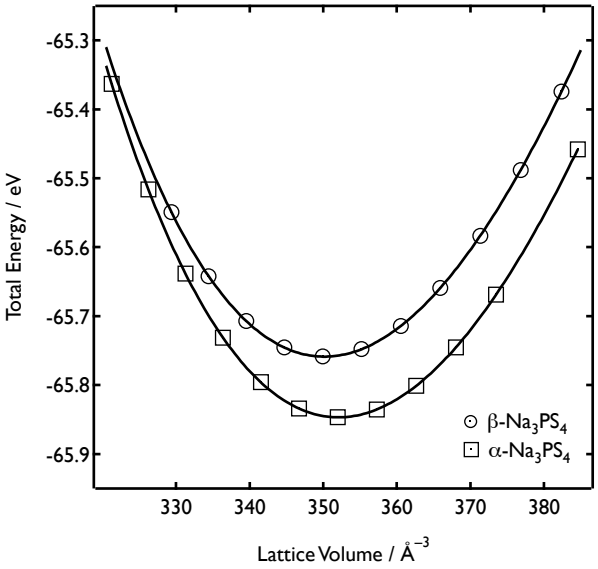

Figure S3 Total energy versus lattice volume for α- and β-Na_3PS_4.

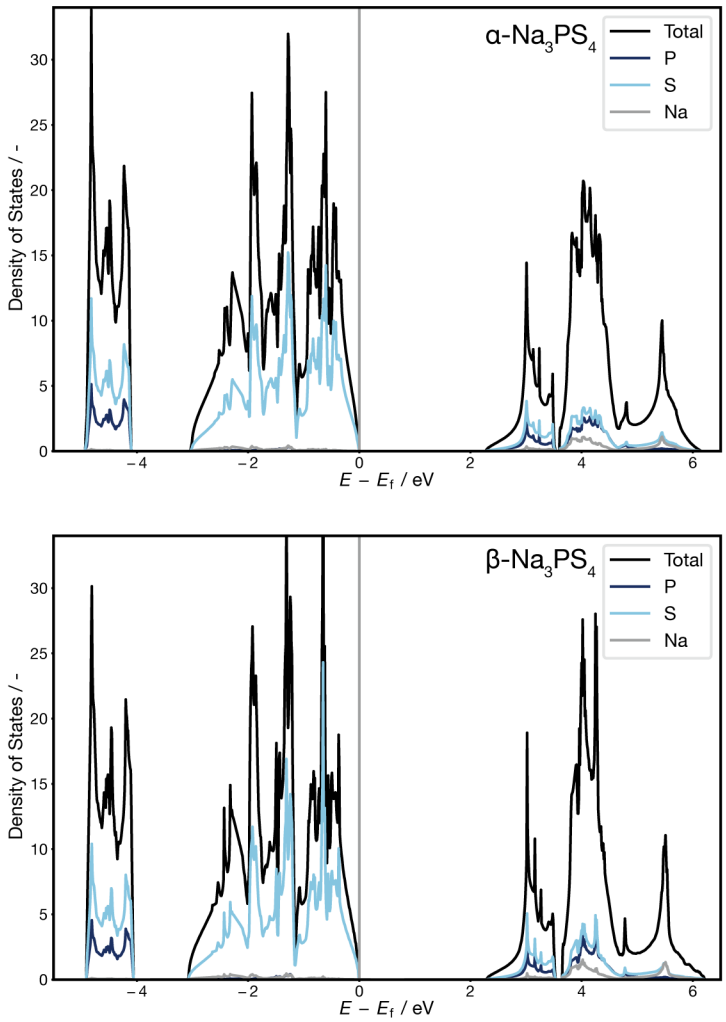

Figure S4 Electronic density of states of states of α- and β-Na_3PS_4.

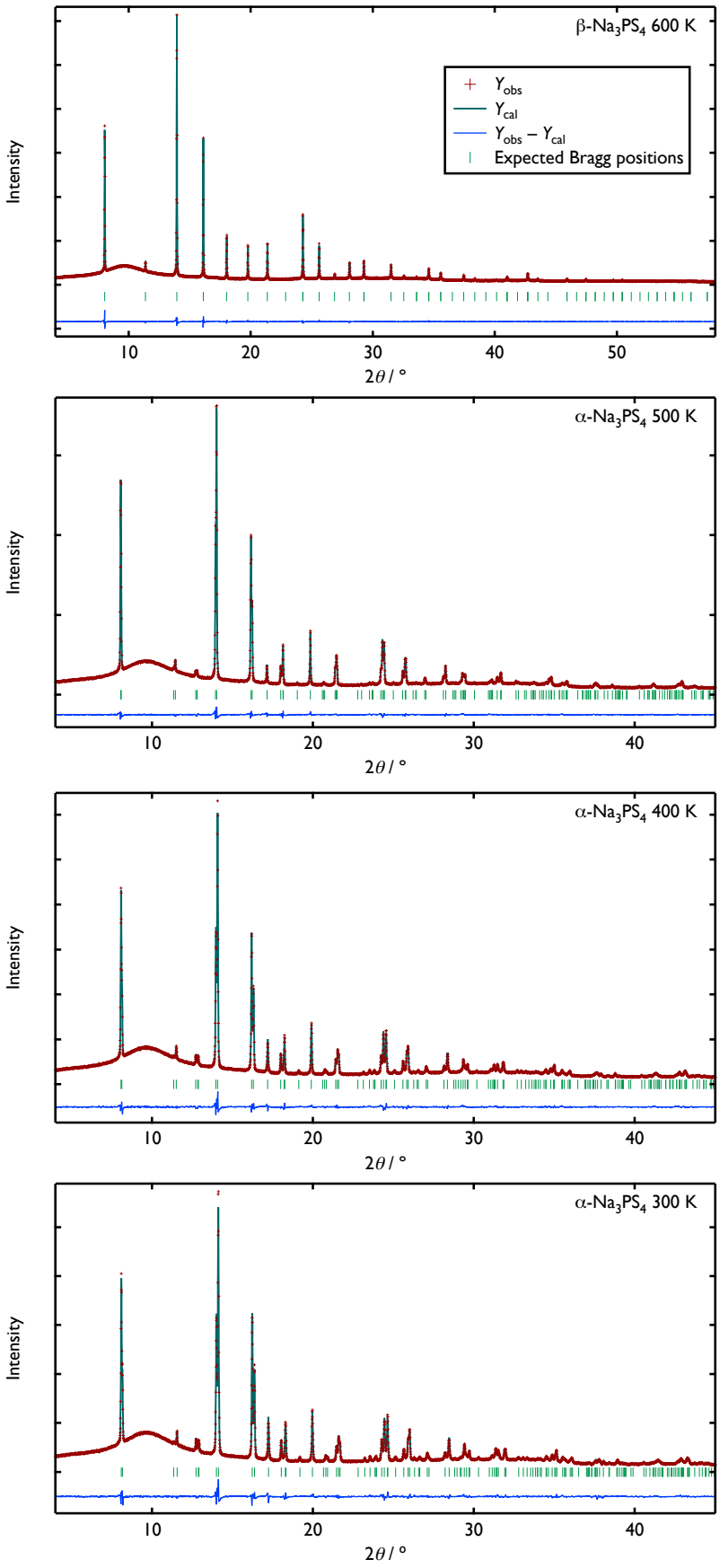

Figure S5 Rietveld refinement patterns of Na_3PS_4 at 300, 400, 500, and 600 K.

Table S1 Crystal data for α-Na_3PS_4 at 300 K and β-Na_3PS_4 at 600 K.

Chemical formula	Na_3PS_4	
Z	2	
Mr	228.20	
T (K)	300	600
Crystal system	Tetragonal	Cubic
Space group	$P\bar{4}2_1c$	$I\bar{4}3m$
a (Å)	6.9587(13)	7.06985(4)
c (Å)	7.0832(9)	–
V (Å^3)	342.99(12)	353.370(7)
R_{wp}	0.0364	0.0293
R_p	0.0264	0.0221
R_{Bragg}	0.0158	0.00678

Table S2 Fractional coordinates, isotropic atomic displacement parameters (ADPs) and occupancies for α-Na_3PS_4 at 300 K.

	x	y	z	B_{iso} (Å^2)
Na1	0	1/2	0.4281 (4)	
Na2	0	0	0	
P	0	0	1/2	1.14 (5)
S	0.31409 (17)	0.34547 (15)	0.16605 (18)	

Table S3 Anisotropic ADPs for α-Na_3PS_4 at 300 K. (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.045 (3)	0.017 (2)	0.086 (3)	0	0	0
Na2	0.092 (3)	= U^{11}	0.011 (3)	0	0	0
S1	0.0261 (12)	0.0169 (12)	0.0259 (8)	–0.0054 (8)	0.0044 (11)	–0.0011 (11)

Table S4 Fractional coordinates, isotropic ADPs and occupancies for β-Na_3PS_4 at 600 K.

	x	y	z	B_{iso} (Å^2)	Occ. (<1)
Na	0.0626 (14)	0	1/2		1/4
P	0	0	0	2.25 (3)	
S	0.16738 (6)	= x	= x		

Table S5 Anisotropic ADPs for β-Na_3PS_4 at 600 K. (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0484 (3)	= U^{11}	= U^{11}	–0.0107 (4)	= U^{12}	= U^{12}
Na	0.110 (6)	0.098 (7)	0.0418 (18)	0	0	0