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SUPPORTING INFORMATION

$Na_7V_3(P_2O_7)_4$ as a high voltage electrode material for Na-ion batteries: crystal structure and mechanism of Na^+ extraction/insertion by *operando* X-ray diffraction

Vadim M. Kovrugin,[ab] Jean-Noël Chotard,[ab] François Fauth,[c] and Christian Masquelier*[ab]

[a] Laboratoire de Réactivité et de Chimie des Solides (LRCS), UMR 7314, Université de Picardie Jules Verne, 80039 Amiens Cedex, France

[b] RS2E, Réseau Français sur le Stockage Electrochimique de l'Energie, FR CNRS 3459, 80039 Amiens Cedex, France

[c] CELLS – ALBA Synchrotron, 08290 Cerdanyola del Valles, Barcelona, Spain

Corresponding author: christian.masquelier@u-picardie.fr

Table of Contents

S1. Single crystal XRD data

Table S1. Atomic anisotropic displacement parameters (Å^2) in the crystal structure of $Na_7V_3(P_2O_7)_4$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P1	0.0059(5)	0.0082(6)	0.0065(6)	−0.0021(5)	−0.0011(4)	0.0023(5)
P2	0.0065(5)	0.0088(6)	0.0059(6)	−0.0001(5)	−0.0006(4)	0.0006(5)
P3	0.0043(5)	0.0050(6)	0.0076(6)	0.0004(4)	0.0007(4)	0.0005(5)
P4	0.0036(5)	0.0044(6)	0.0065(6)	−0.0006(4)	−0.0001(4)	0.0006(5)
V1	0.0045(4)	0.0050(6)	0.0062(6)	0	−0.0004(4)	0
V2	0.0036(3)	0.0047(4)	0.0069(4)	0.0002(3)	0.0004(3)	0.0008(3)
O1	0.0116(14)	0.0145(18)	0.0125(18)	−0.0009(13)	0.0045(13)	−0.0014(15)
O2	0.0089(13)	0.0075(17)	0.0113(18)	−0.0010(13)	0.0006(12)	−0.0001(13)
O3	0.0069(13)	0.0085(17)	0.0142(19)	−0.0009(13)	−0.0014(13)	0.0015(14)
O4	0.0043(13)	0.0062(16)	0.0093(17)	−0.0001(12)	−0.0005(12)	0.0051(13)
O5	0.0059(13)	0.0177(18)	0.0074(17)	−0.0017(13)	−0.0011(12)	0.0009(14)
O6	0.0213(16)	0.0091(17)	0.0149(19)	0.0002(14)	0.0027(14)	−0.0012(15)
O7	0.0135(14)	0.0116(18)	0.0061(17)	−0.0001(13)	−0.0019(12)	0.0035(14)
O8	0.0062(13)	0.0078(16)	0.0103(17)	0.0012(12)	0.0005(12)	0.0009(14)
O9	0.0061(13)	0.0085(17)	0.0125(18)	−0.0006(13)	0.0005(12)	0.0015(14)
O10	0.0097(13)	0.0112(17)	0.0095(17)	0.0006(13)	0.0002(12)	−0.0014(14)
O11	0.0091(13)	0.0045(15)	0.0051(15)	−0.0001(12)	0.0030(12)	0.0005(13)
O12	0.0084(13)	0.0052(16)	0.0067(17)	0.0023(12)	−0.0016(12)	0.0001(13)
O13	0.0062(13)	0.0086(16)	0.0124(18)	−0.0027(13)	−0.0025(12)	0.0004(14)
O14	0.0075(13)	0.0076(16)	0.0127(17)	−0.0030(12)	0.0032(12)	−0.0009(14)
Na1	0.0193(9)	0.0096(10)	0.0272(12)	−0.0046(8)	0.0111(8)	−0.0061(9)
Na2A	0.070(15)	0.025(8)	0.015(6)	−0.002(6)	0.009(7)	−0.010(5)
Na2B	0.046(5)	0.026(7)	0.026(6)	−0.023(7)	0.022(5)	−0.009(5)
Na3A	0.021(2)	0.009(3)	0.083(5)	0	0.015(3)	0
Na3B	0.031(6)	0.005(5)	0.093(11)	0.002(4)	−0.014(5)	−0.019(6)
Na3C	0.018(9)	0.044(14)	0.043(14)	0.010(9)	−0.022(8)	−0.025(10)
Na4A	0.036(4)	0.031(5)	0.027(5)	0.012(4)	−0.011(3)	0.015(4)
Na4B	0.039(3)	0.042(3)	0.018(3)	0.019(3)	−0.006(2)	−0.001(3)

Table S2. Selected interatomic distances for Na sites in the crystal structure of $Na_7V_3(P_2O_7)_4$

Distance	Å	Distance	Å
Na1—O10	2.256(3)	Na3B—O1	2.407(10)
Na1—O9	2.312(3)	Na3B—O3	2.469(11)
Na1—O12	2.358(3)	Na3B—O6	2.614(11)
Na1—O6	2.375(4)	Na3B—O4	2.634(10)
Na1—O13	2.497(3)	Na3B—O3	2.710(12)
Na1—O8	2.783(3)	Na3B—O5	2.870(10)
Na1—O9	2.879(4)	Na3B—O7	2.966(11)
<Na1—O>	2.432	<Na3B—O>	2.667
Na2A—O1	2.34(4)	Na3C—O3	2.426(19)
Na2A—O10	2.40(4)	Na3C—O7	2.447(17)
Na2A—O14	2.52(5)	Na3C—O6	2.545(17)
Na2A—O5	2.55(4)	Na3C—O5	2.56(2)
Na2A—O6	2.70(4)	Na3C—O8	2.66(2)
Na2A—O13	2.83(3)	Na3C—O4	2.85(2)
Na2A—O7	2.84(3)	<Na3C—O>	2.58
<Na2A—O>	2.60		
		Na4A—O1	2.279(7)
Na2B—O10	2.30(2)	Na4A—O10	2.311(7)
Na2B—O5	2.43(2)	Na4A—O6	2.434(9)
Na2B—O1	2.46(2)	Na4A—O2	2.597(9)
Na2B—O6	2.52(2)	Na4A—O5	2.792(7)
Na2B—O2	2.73(3)	Na4A—O3	2.891(8)
Na2B—O14	2.75(3)	<Na4A—O>	2.551
Na2B—O4	2.92(2)		
Na2B—O13	2.94(2)	Na4B—O10	2.428(6)
Na2B—O7	2.97(2)	Na4B—O1	2.456(5)
<Na2B—O>	2.67	Na4B—O3	2.538(6)
		Na4B—O7	2.549(6)
Na3A—O3 x2	2.302(5)	Na4B—O8	2.597(6)
Na3A—O1 x2	2.419(5)	Na4B—O5	2.617(5)
Na3A—O4 x2	2.443(4)	Na4B—O14	2.792(5)
<Na3A—O>	2.388	<Na4B—O>	2.568
NA2A—NA2B	0.283(11)	NA3A—NA3B	1.740(13)
		NA3B—NA3C	0.857(19)
NA4A—NA4B	1.147(8)	NA3A—NA3C	2.45(2)

Table S3. Selected interatomic distances for V and P sites in the crystal structure of $Na_7V_3(P_2O_7)_4$

Distance	**Å**	**Distance**	**Å**
P1—O1	1.497(3)	P4—O13	1.511(3)
P1—O2	1.517(3)	P4—O14	1.514(3)
P1—O3	1.530(3)	P4—O12	1.516(3)
P1—O4	1.633(3)	P4—O11	1.586(3)
<P1—O>	1.544	<P4—O>	1.532
P2—O6	1.481(3)	V1—O5 x2	1.965(3)
P2—O7	1.522(3)	V1—O2 x2	2.011(3)
P2—O5	1.541(3)	V1—O3 x2	2.069(3)
P2—O4	1.619(3)	<V1—O>	2.015
<P2—O>	1.541		
		V2—O7	1.986(3)
P3—O10	1.489(3)	V2—O12	1.996(3)
P3—O8	1.523(3)	V2—O8	2.007(3)
P3—O9	1.526(3)	V2—O13	2.009(3)
P3—O11	1.615(3)	V2—O9	2.030(3)
<P3—O>	1.538	V2—O14	2.041(3)
		<V2—O>	2.012

S2. Electrochemical data

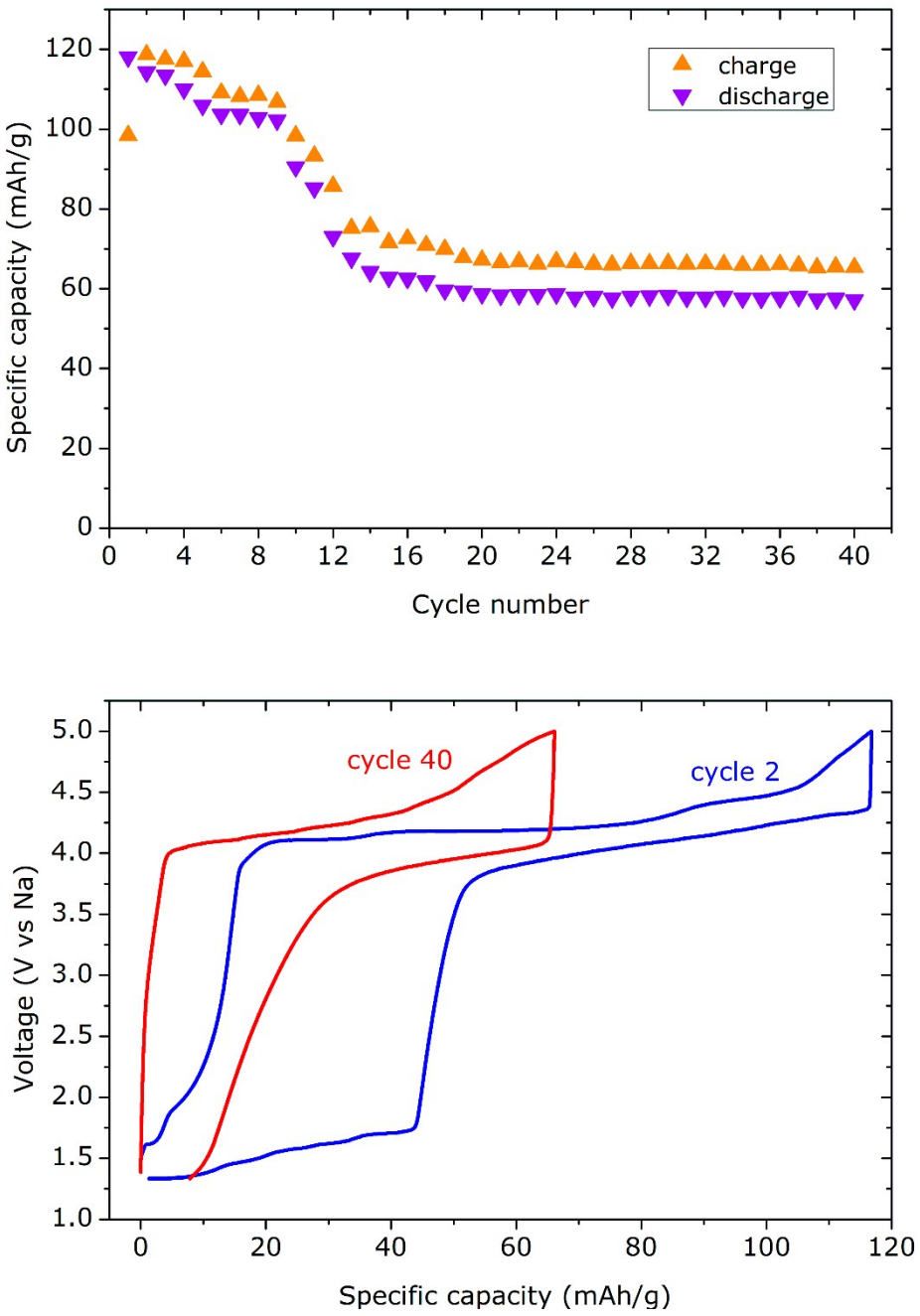

Figure S1. Long-term cycling performance (top); the second and fiftieth cycle of galvanostatic data for $Na_7V_3(P_2O_7)_4$ at 3 Na^+/18 h cycled between 1.35 and 5.0 V vs. Na^+/Na (down).

S3. *In situ* XRD experiment

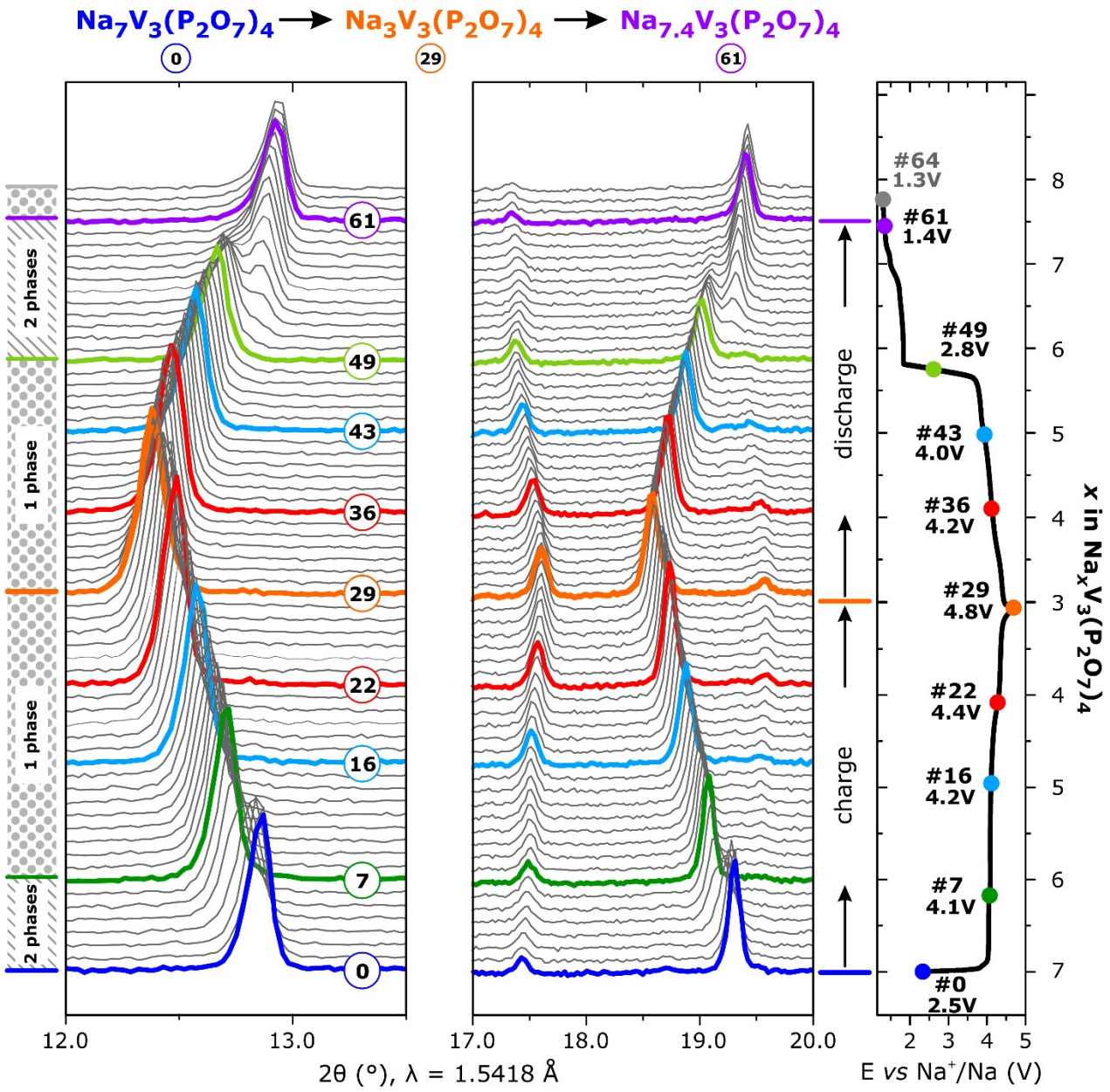

Figure S2. *In situ* XRD patterns recorded *operando* for the $Na_7V_3(P_2O_7)_4$ electrode upon charge and discharge between 1.3 and 4.8 V *vs.* Na^+/Na.

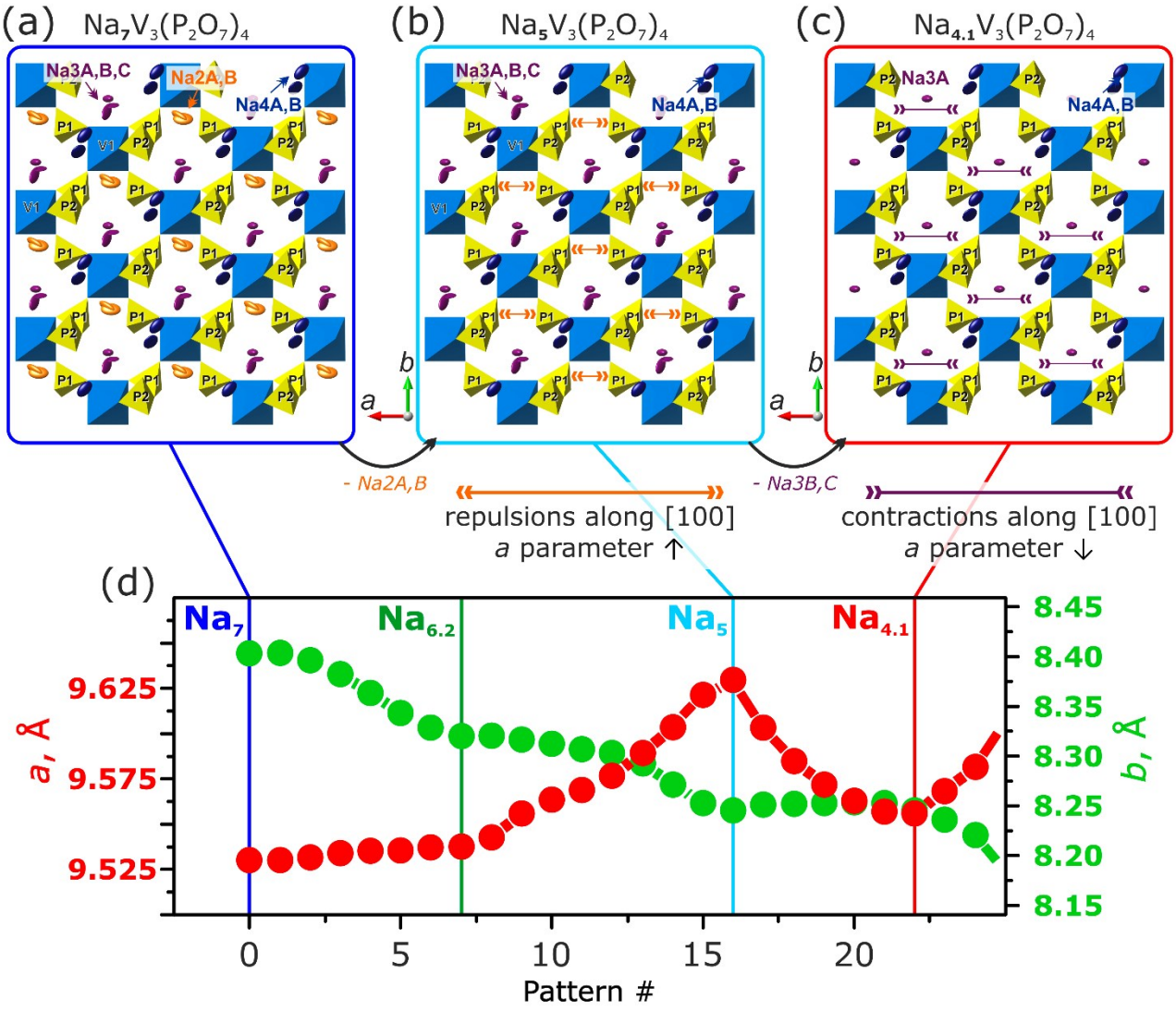

Figure S3. Projections of the crystal structures of $Na_7V_3(P_2O_7)_4$ (a), $Na_5V_3(P_2O_7)_4$ (b), and $Na_{4.1}V_3(P_2O_7)_4$ (c) along the *c* axis; Na2, Na3, and Na4 are shown by orange, purple and dark blue thermal ellipsoids (drawn at 90% probability level), respectively. Variation of the *a* and *b* parameters obtained upon Na+ extraction – (d)

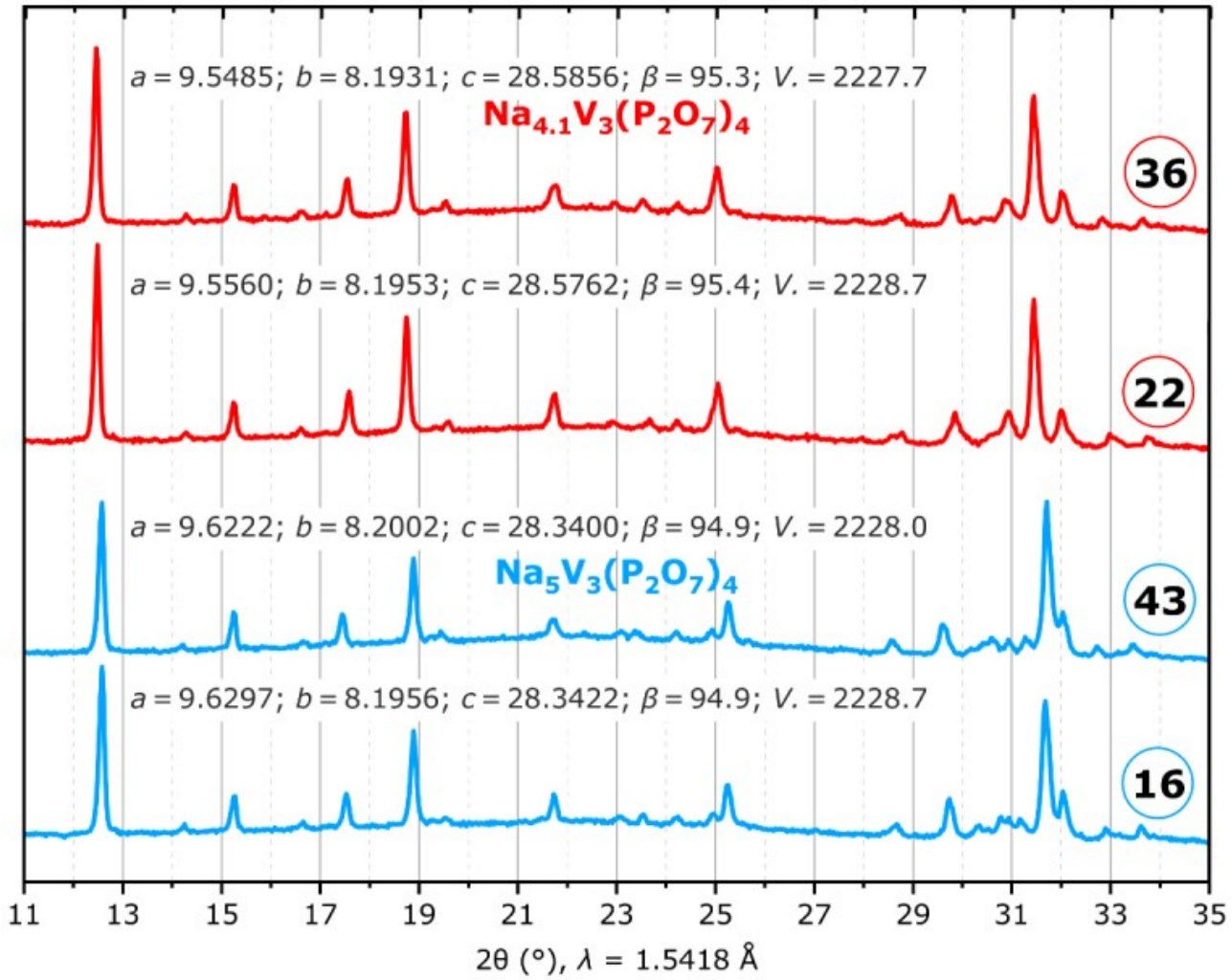

Figure S4. *In situ* XRD patterns and lattice parameters of the $Na_5V_3(P_2O_7)_4$ (blue) and $Na_{4.1}V_3(P_2O_7)_4$ (red) phases obtained upon charging and discharging.

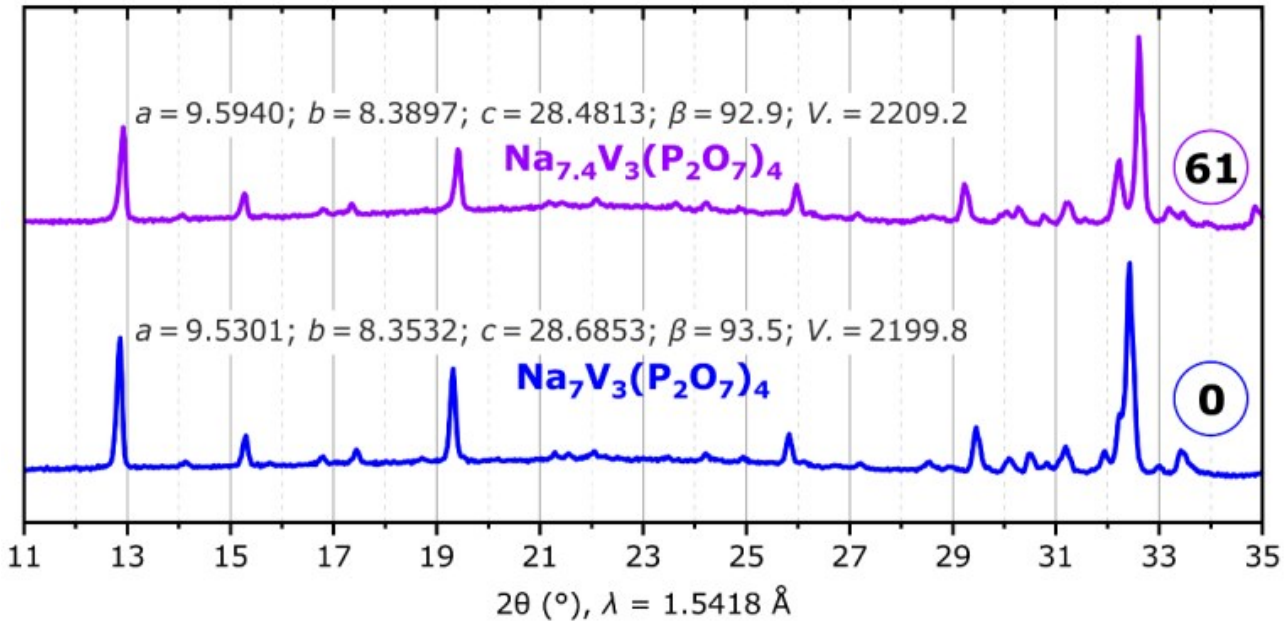

Figure S5. *In situ* XRD patterns and lattice parameters of the pristine $Na_7V_3(P_2O_7)_4$ (blue) and $Na_{7.4}V_3(P_2O_7)_4$ (purple) phases.

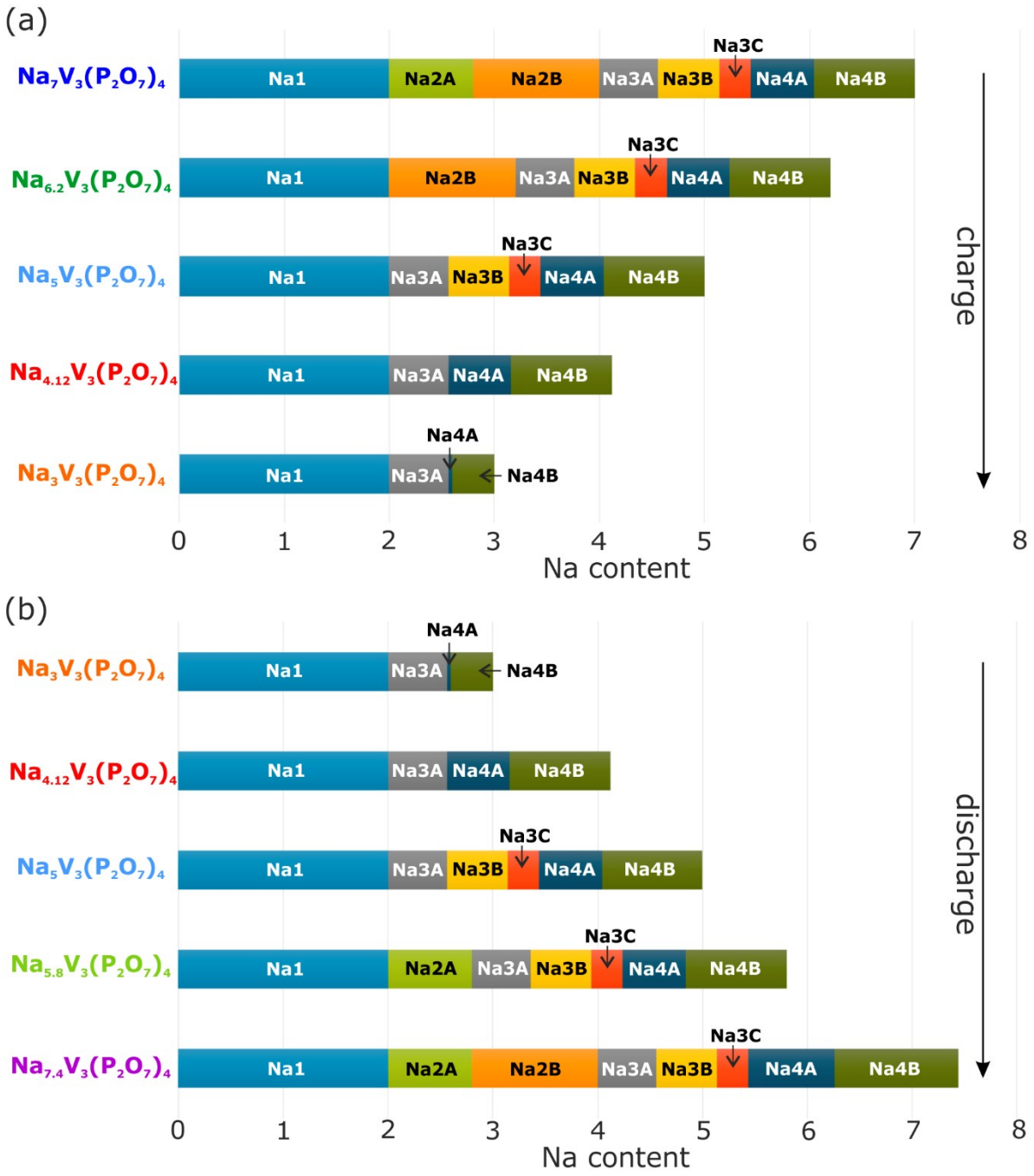

Figure S6. Theoretical occupancies of Na sites in different $Na_xV_3(P_2O_7)_4$ compositions.

Table S4. Lattice parameters obtained upon Na^+ extraction/insertion from/into the structure of $Na_xV_3(P_2O_7)_4$ compositions

Pattern #	Na_x	*a* [Å]	*b* [Å]	*c* [Å]	β [°]	Vol. [Å^3]
0	**7.0**	9.5301(8)	8.3532(8)	27.6853(4)	93.511(7)	2199.8(3)
7	**6.2**	9.5376(7)	8.2701(9)	28.0240(9)	94.187(7)	2204.5(3)
16	**5.0**	9.630(1)	8.196(1)	28.342(1)	94.88(1)	2228.7(4)
22	**4.12**	9.5560(7)	8.1953(7)	28.576(1)	95.36(1)	2228.1(3)
29	**3.0**	9.696(1)	8.0330(9)	28.813(1)	95.532(8)	2233.8(3)
36	**4.12**	9.5485(6)	8.1931(9)	28.586(1)	95.332(9)	2226.7(3)
43	**5.0**	9.622(1)	8.200(1)	28.340(1)	94.88(1)	2228.0(4)
49	**5.8**	9.5680(5)	8.3253(7)	28.0556(8)	93.868(5)	2229.7(2)
61	**7.4**	9.594(1)	8.3897(8)	27.4813(5)	92.878(6)	2209.2(3)