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

Supplementary Information

Structural and electrochemical studies of novel $Na_7V_3Al(P_2O_7)_4(PO_4)$ and $Na_7V_2Al_2(P_2O_7)_4(PO_4)$ high-voltage cathode materials for Na-ion batteries

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S1. Powder X-ray diffraction patterns of the obtained solid products

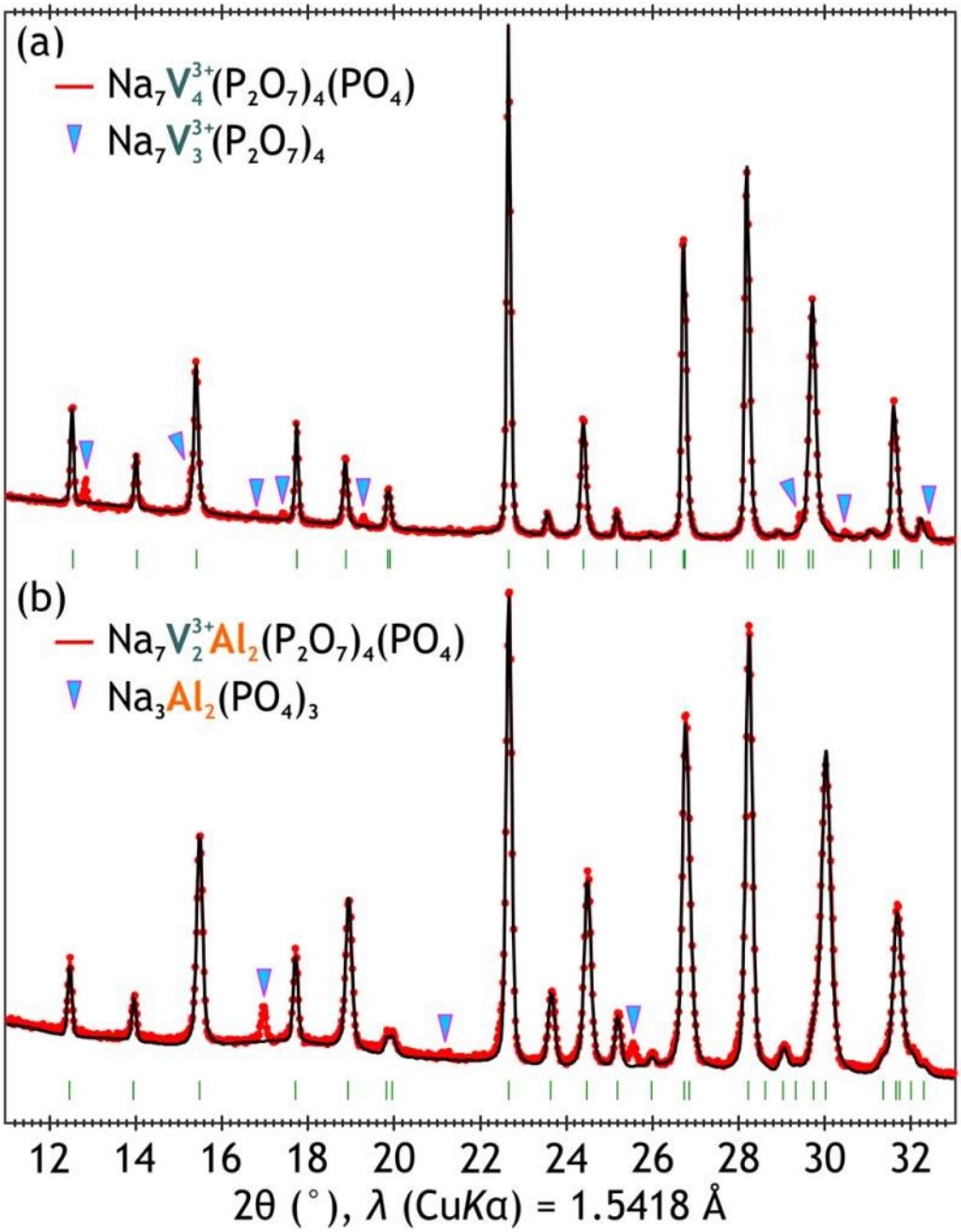

Figure S1 | Results of the Rietveld refinements of the crystal structures of new $Na_7V_3Al(P_2O_7)_4(PO_4)$ (a) and $Na_7V_2Al_2(P_2O_7)_4(PO_4)$ (b) based on laboratory powder XRD data.

S2. Rietveld refinement of the powder X-ray diffraction data

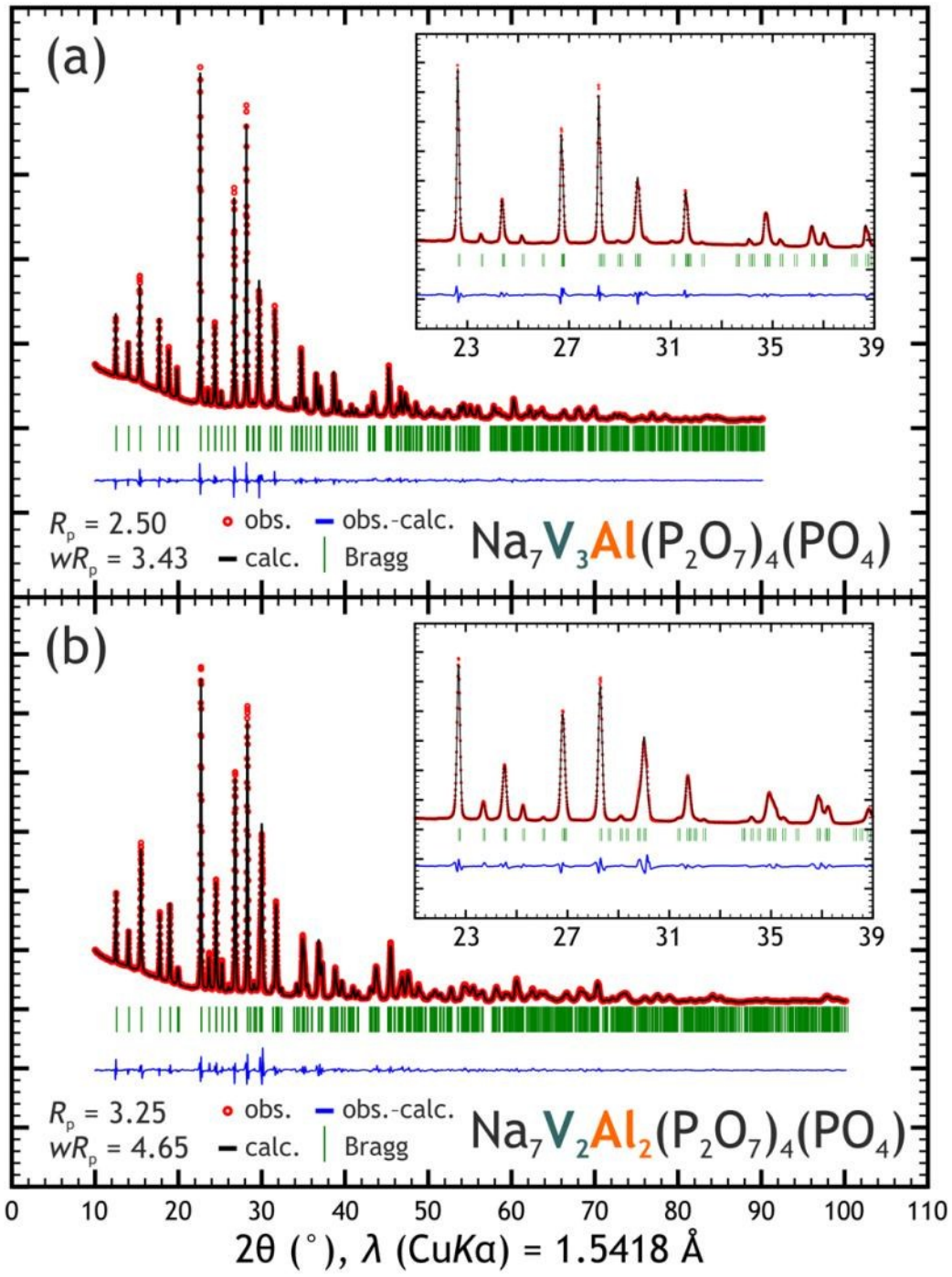

Figure S2 | Results of the Rietveld refinement of the structures of new $Na_7V_3Al(P_2O_7)_4(PO_4)$ (a) and $Na_7V_2Al_2(P_2O_7)_4(PO_4)$ from the laboratory powder XRD data.

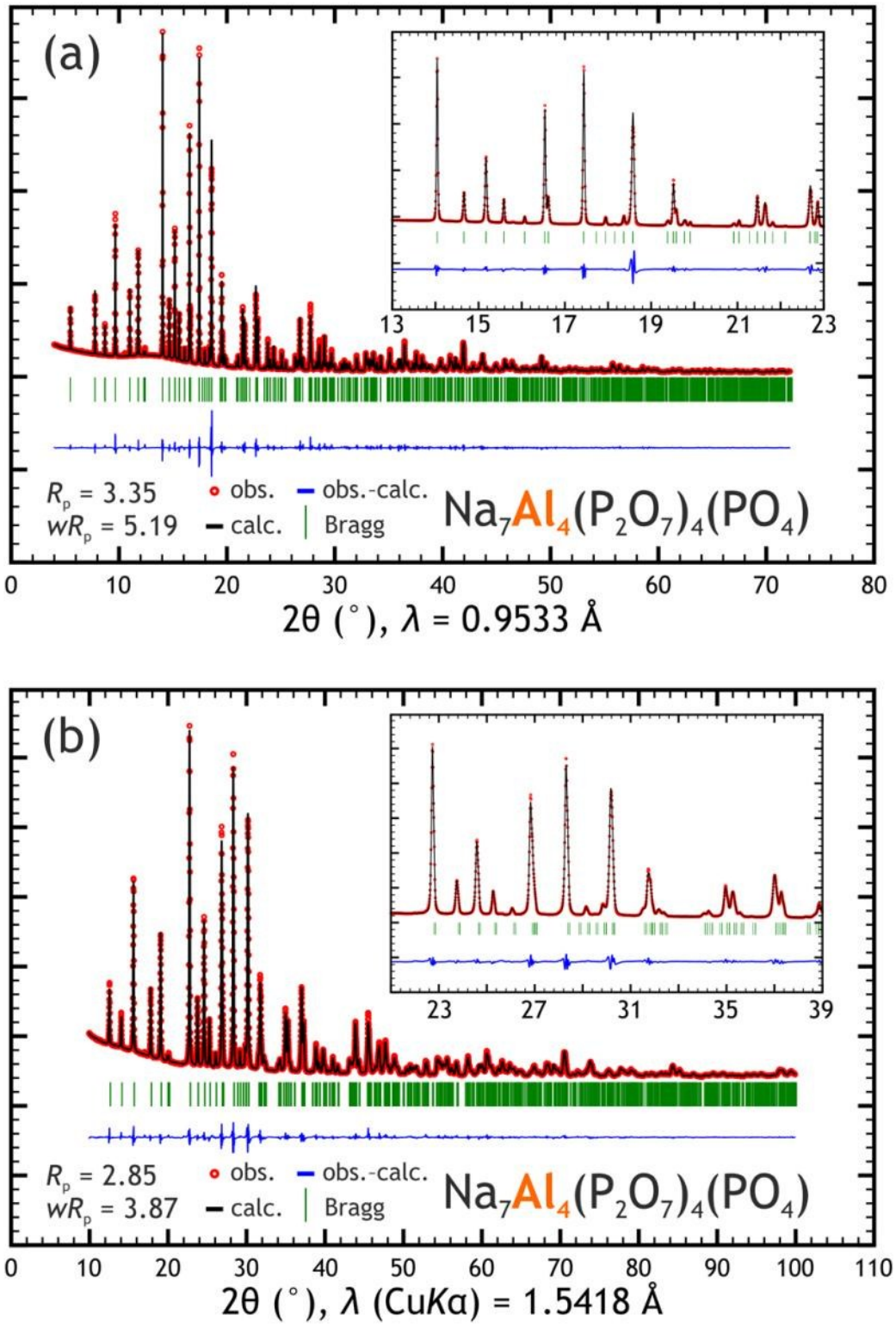

Figure S3 | Results of the Rietveld refinement of the crystal structure of $Na_7Al_4(P_2O_7)_4(PO_4)$ from the synchrotron (a) and laboratory (b) powder XRD data.

S3. Single crystal X-ray diffraction data

Table S1 | Fractional atomic coordinates and equivalent displacement parameters (Å^2) for $Na_7V_4(P_2O_7)_4(PO_4)$.

	Wyck.	*x*	*y*	*z*	U_{eq}
V1	8e	0.81624(4)	0.12034(4)	0.12976(11)	0.00596(14)
P1	2a	0	0	0	0.0057(4)
P2	8e	0.61985(7)	0.25690(7)	0.14137(15)	0.00642(19)
P3	8e	0.95619(7)	0.30282(7)	0.11002(17)	0.00721(19)
NA1	2b	0	0	1/2	0.0619(16)
NA2	4d	0	1/2	0.8278(4)	0.0287(7)
NA3	8e	0.91816(13)	0.25935(13)	0.6041(3)	0.0200(4)
O1	8e	0.13703(19)	0.17101(19)	0.1884(4)	0.0104(6)
O2	8e	0.6995(2)	0.1912(2)	0.1025(5)	0.0177(6)
O3	8e	0.93538(18)	0.05554(19)	0.1477(4)	0.0104(6)
O4	8e	0.5359(2)	0.1880(2)	0.2107(5)	0.0151(6)
O5	8e	0.5864(2)	0.3048(2)	0.9432(4)	0.0149(7)
O6	8e	0.0020(2)	0.2570(2)	0.9201(4)	0.0115(6)
O7	8e	0.9269(2)	0.40252(19)	0.0722(5)	0.0138(6)
O8	8e	0.8796(2)	0.2434(2)	0.2074(5)	0.0173(7)

Table S2 | Fractional atomic coordinates and isotropic or equivalent displacement parameters (Å^2) for $Na_7V_3Al(P_2O_7)_4(PO_4)$.

	Wyck.	*x*	*y*	*z*	U_{eq}/U_{iso}*
*M*1 ($V_{0.75}Al_{0.25}$)	8e	0.81757(12)	0.12096(12)	0.1317(3)	0.0090(4)
P1	2a	0	0	0	0.0068(10)
P2	8e	0.62231(17)	0.25698(16)	0.1444(4)	0.0062(5)
P3	8e	0.95720(17)	0.30166(16)	0.1063(4)	0.0068(5)
Na1	2b	0	0	1/2	0.050(3)
Na2	4d	0	1/2	0.8235(9)	0.0277(15)
Na3	8e	0.9187(3)	0.2590(3)	0.6009(7)	0.0195(10)
O1	8e	0.1378(4)	0.1713(4)	0.1843(9)	0.0101(15)*
O2	8e	0.7019(4)	0.1906(5)	0.1096(12)	0.0192(16)
O3	8e	0.9347(4)	0.0542(4)	0.1483(10)	0.0087(13)
O4	8e	0.5355(4)	0.1898(5)	0.2112(11)	0.0188(17)
O5	8e	0.5903(5)	0.3056(5)	0.9447(10)	0.0171(17)
O6	8e	0.0034(5)	0.2561(4)	0.9175(10)	0.0107(14)
O7	8e	0.9269(4)	0.4017(4)	0.0690(10)	0.0105(16)
O8	8e	0.8802(5)	0.2421(5)	0.2030(10)	0.0179(16)

Table S3 | Fractional atomic coordinates and equivalent displacement parameters (Å^2) for $Na_7V_2Al_2(P_2O_7)_4(PO_4)$.

	Wyck.	*x*	*y*	*z*	U_{eq}
*M*1 ($V_{0.5}Al_{0.5}$)	8e	0.81818(16)	0.12135(17)	0.1333(2)	0.0095(5)
P1	2a	0	0	0	0.0068(12)
P2	8e	0.6239(2)	0.2570(2)	0.1458(3)	0.0078(6)
P3	8e	0.95804(19)	0.30135(19)	0.1052(3)	0.0090(6)
Na1	2b	0	0	1/2	0.055(4)
Na2	4d	0	1/2	0.8213(6)	0.0310(19)
Na3	8e	0.9197(3)	0.2585(3)	0.5988(5)	0.0240(12)
O1	8e	0.1371(5)	0.1706(6)	0.1807(7)	0.016(2)
O2	8e	0.7032(5)	0.1914(5)	0.1133(8)	0.0194(19)
O3	8e	0.9326(5)	0.0533(5)	0.1488(8)	0.0131(17)
O4	8e	0.5373(5)	0.1890(6)	0.2104(8)	0.0174(19)
O5	8e	0.5913(6)	0.3071(5)	0.9431(7)	0.018(2)
O6	8e	0.0067(5)	0.2558(5)	0.9148(7)	0.0130(17)
O7	8e	0.9278(5)	0.4004(5)	0.0669(7)	0.0117(18)
O8	8e	0.8813(7)	0.2410(6)	0.2020(8)	0.022(2)

Table S4 | Atomic displacement parameters (Å^2) for $Na_7V_4(P_2O_7)_4(PO_4)$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V1	0.0058(3)	0.0062(3)	0.0059(3)	0.0006(2)	0.0004(3)	−0.0005(3)
P1	0.0056(5)	0.0056(5)	0.0061(9)	0.000	0.000	0.000
P2	0.0065(4)	0.0076(4)	0.0052(4)	0.0003(4)	0.0003(4)	0.0003(4)
P3	0.0071(4)	0.0070(4)	0.0075(5)	0.0008(3)	−0.0007(4)	−0.0004(4)
NA1	0.085(3)	0.085(3)	0.016(2)	0.000	0.000	0.000
NA2	0.0300(15)	0.0440(17)	0.0121(13)	−0.0242(12)	0.000	0.000
NA3	0.0212(9)	0.0224(9)	0.0163(9)	−0.0044(7)	−0.0028(8)	0.0033(8)
O1	0.0143(15)	0.0101(14)	0.0067(13)	0.0049(11)	−0.0015(11)	0.0006(11)
O2	0.0136(14)	0.0231(16)	0.0164(16)	0.0098(11)	−0.0013(13)	−0.0033(14)
O3	0.0085(12)	0.0138(13)	0.0091(13)	0.0052(10)	−0.0017(12)	−0.0026(12)
O4	0.0152(15)	0.0185(15)	0.0114(14)	−0.0106(13)	0.0071(12)	−0.0061(13)
O5	0.0209(16)	0.0175(15)	0.0064(14)	0.0066(13)	−0.0004(12)	0.0020(12)
O6	0.0112(13)	0.0144(14)	0.0089(14)	0.0030(11)	−0.0018(12)	−0.0031(12)
O7	0.0186(15)	0.0097(14)	0.0133(15)	0.0031(12)	−0.0021(12)	0.0006(11)
O8	0.0172(15)	0.0152(15)	0.0194(15)	−0.0089(13)	0.0076(13)	−0.0074(13)

Table S5 | Atomic displacement parameters (Å^2) for $Na_7V_3Al(P_2O_7)_4(PO_4)$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
*M*1 ($V_{0.75}Al_{0.25}$)	0.0109(10)	0.0082(9)	0.0081(9)	−0.0006(8)	0.0005(9)	0.0002(9)
P1	0.0100(17)	0.0100(17)	0.001(2)	0.000	0.000	0.000
P2	0.0071(12)	0.0054(12)	0.0060(11)	0.0004(11)	0.0005(11)	0.0024(11)
P3	0.0066(12)	0.0056(12)	0.0081(12)	0.0024(10)	−0.0009(10)	0.0006(10)
Na1	0.070(4)	0.070(4)	0.009(4)	0.000	0.000	0.000
Na2	0.028(3)	0.040(4)	0.015(3)	−0.021(3)	0.000	0.000
Na3	0.023(2)	0.021(2)	0.015(2)	−0.0045(19)	−0.0009(19)	0.004(2)
O2	0.011(4)	0.026(4)	0.021(4)	0.012(3)	0.000(3)	−0.004(4)
O3	0.005(3)	0.015(3)	0.006(3)	0.003(3)	−0.001(3)	−0.004(3)
O4	0.014(4)	0.021(4)	0.022(4)	−0.015(3)	0.010(3)	−0.011(3)
O5	0.025(4)	0.018(4)	0.008(4)	0.008(4)	−0.002(3)	0.002(3)
O6	0.012(3)	0.012(3)	0.008(3)	0.007(3)	−0.001(3)	−0.003(3)
O7	0.015(4)	0.003(3)	0.013(4)	0.003(3)	−0.001(3)	−0.002(3)
O8	0.019(4)	0.018(4)	0.017(4)	−0.003(4)	0.006(3)	−0.004(3)

Table S6 | Atomic displacement parameters (Å^2) for $Na_7V_2Al_2(P_2O_7)_4(PO_4)$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
*M*1 ($V_{0.5}Al_{0.5}$)	0.0112(14)	0.0109(13)	0.0063(9)	0.0019(12)	0.0005(8)	0.0007(9)
P1	0.006(2)	0.006(2)	0.008(2)	0.000	0.000	0.000
P2	0.0057(15)	0.0091(17)	0.0086(10)	−0.0004(13)	0.0008(10)	0.0010(10)
P3	0.0072(16)	0.0098(16)	0.0099(10)	0.0022(12)	−0.0019(9)	−0.0008(10)
Na1	0.072(6)	0.072(6)	0.020(4)	0.000	0.000	0.000
Na2	0.035(5)	0.047(5)	0.011(3)	−0.031(5)	0.000	0.000
Na3	0.027(3)	0.029(3)	0.0154(15)	−0.010(2)	−0.0051(17)	0.0026(18)
O1	0.020(5)	0.020(5)	0.008(3)	0.002(4)	−0.001(3)	0.001(3)
O2	0.026(5)	0.022(5)	0.011(3)	0.007(4)	0.008(3)	−0.003(3)
O3	0.011(4)	0.021(5)	0.007(3)	0.005(4)	0.001(3)	−0.005(3)
O4	0.008(5)	0.024(5)	0.020(3)	−0.005(4)	0.010(3)	−0.013(3)
O5	0.029(6)	0.018(5)	0.009(3)	0.001(4)	−0.003(3)	0.003(3)
O6	0.014(4)	0.019(5)	0.006(3)	0.002(4)	0.001(3)	−0.001(3)
O7	0.022(5)	0.005(5)	0.008(3)	0.001(4)	−0.004(3)	0.003(2)
O8	0.027(5)	0.020(5)	0.020(3)	−0.009(5)	0.011(3)	−0.005(3)

Table S7 | Selected interatomic distances in the crystal structures of $Na_7V_{4-x}Al_x(P_2O_7)_4(PO_4)$, x = 0, 1, and 2.

Distance, Å	x **= 0**	x **= 1**	x **= 2**
*M*1–O3	1.931(3)	1.911(6)	1.881(7)
*M*1–O2	1.949(3)	1.916(7)	1.904(7)
*M*1–O6	2.003(3)	1.981(7)	1.948(8)
*M*1–O8	2.027(3)	1.987(7)	1.956(8)
*M*1–O1	2.039(3)	2.009(6)	1.981(5)
*M*1–O5	2.051(3)	2.024(6)	1.987(5)
<*M*1–O>	2.000	1.971	1.943
Na1–O3	2.540(3) 4×	2.518(6) 4×	2.507(6) 4×
Na1–O5	3.055(3) 4×	3.052(7) 4×	3.033(8) 4×
<Na1–O>	2.798	2.785	2.770
Na2–O7	2.323(3) 2×	2.322(7) 2×	2.317(7) 2×
Na2–O7	2.371(3) 2×	2.360(7) 2×	2.354(6) 2×
Na2–O4	2.731(3) 2×	2.741(6) 2×	2.725(8) 2×
<Na2–O>	2.475	2.474	2.465
Na3–O6	2.330(3)	2.326(7)	2.325(4)
Na3–O7	2.400(3)	2.397(7)	2.412(9)
Na3–O1	2.521(3)	2.528(7)	2.540(8)
Na3–O5	2.577(4)	2.611(7)	2.606(9)
Na3–O8	2.583(4)	2.573(8)	2.550(6)
Na3–O4	2.709(4)	2.667(8)	2.653(8)
Na3–O8	3.086(4)	3.098(8)	3.127(10)
Na3–O5	3.111(4)	3.036(8)	3.005(9)
<Na3–O>	2.664	2.655	2.652
P1–O3	1.531(3) 4×	1.521(6) 4×	1.528(6) 4×
<P1–O>	1.531	1.521	1.528
P2–O2	1.488(3)	1.482(7)	1.466(7)
P2–O5	1.505(3)	1.496(6)	1.521(6)
P2–O1	1.507(3)	1.503(6)	1.502(7)
P2–O4	1.605(3)	1.608(6)	1.605(7)
<P2–O>	1.526	1.522	1.524
P3–O7	1.496(3)	1.497(6)	1.481(7)
P3–O8	1.510(3)	1.506(7)	1.504(8)
P3–O6	1.516(3)	1.502(7)	1.516(6)
P3–O4	1.609(3)	1.601(6)	1.612(6)
<P3–O>	1.533	1.527	1.528

S4. Energy-dispersive X-ray spectroscopy (EDX) spectra

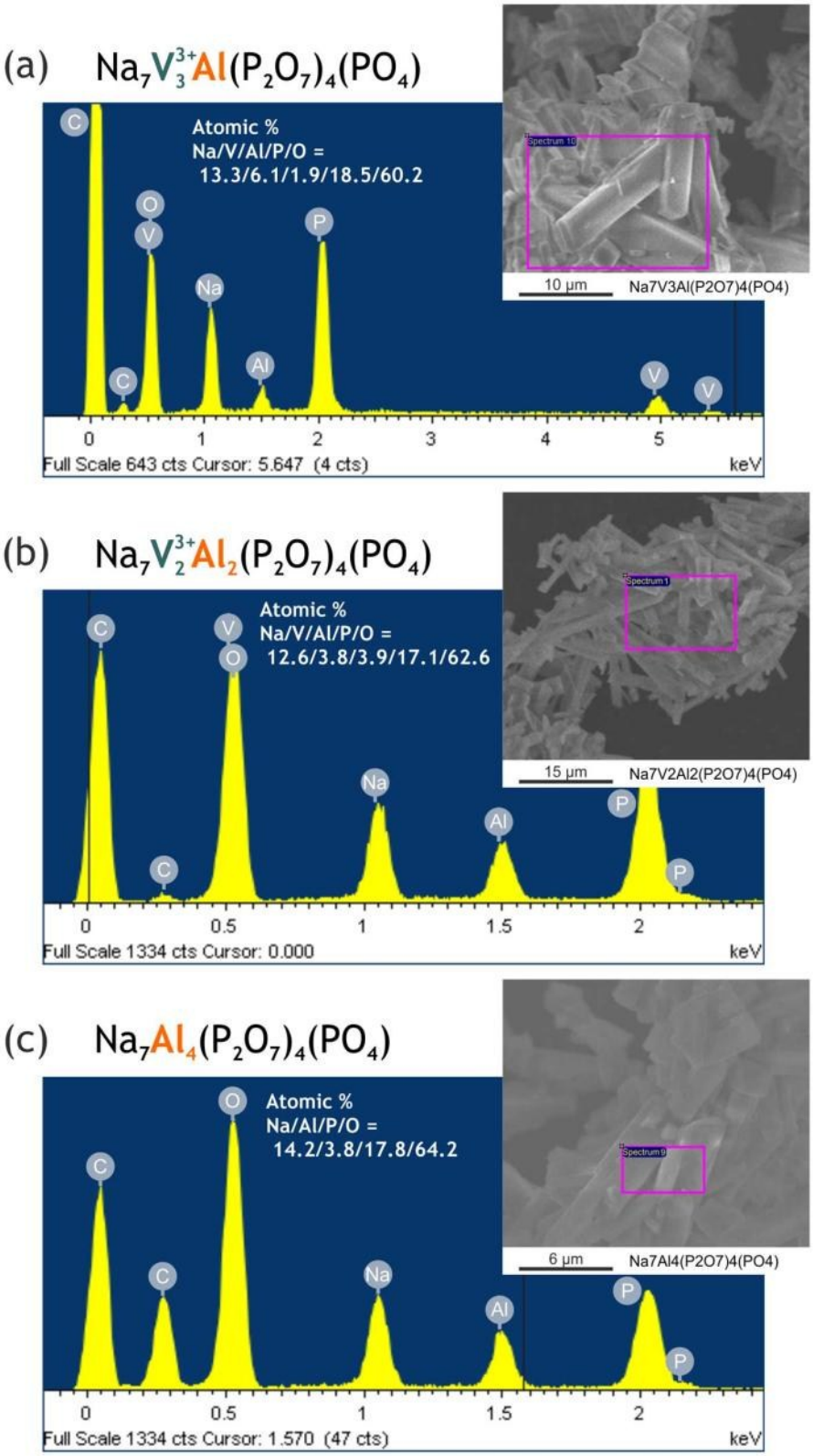

Figure S4 | EDX elemental analysis and SEM image of the powder samples of $Na_7V_{4-x}Al_x(P_2O_7)_4(PO_4)$, x = 1 (a), 2 (b), and 4 (c).

S5. Electrochemical behavior of new materials

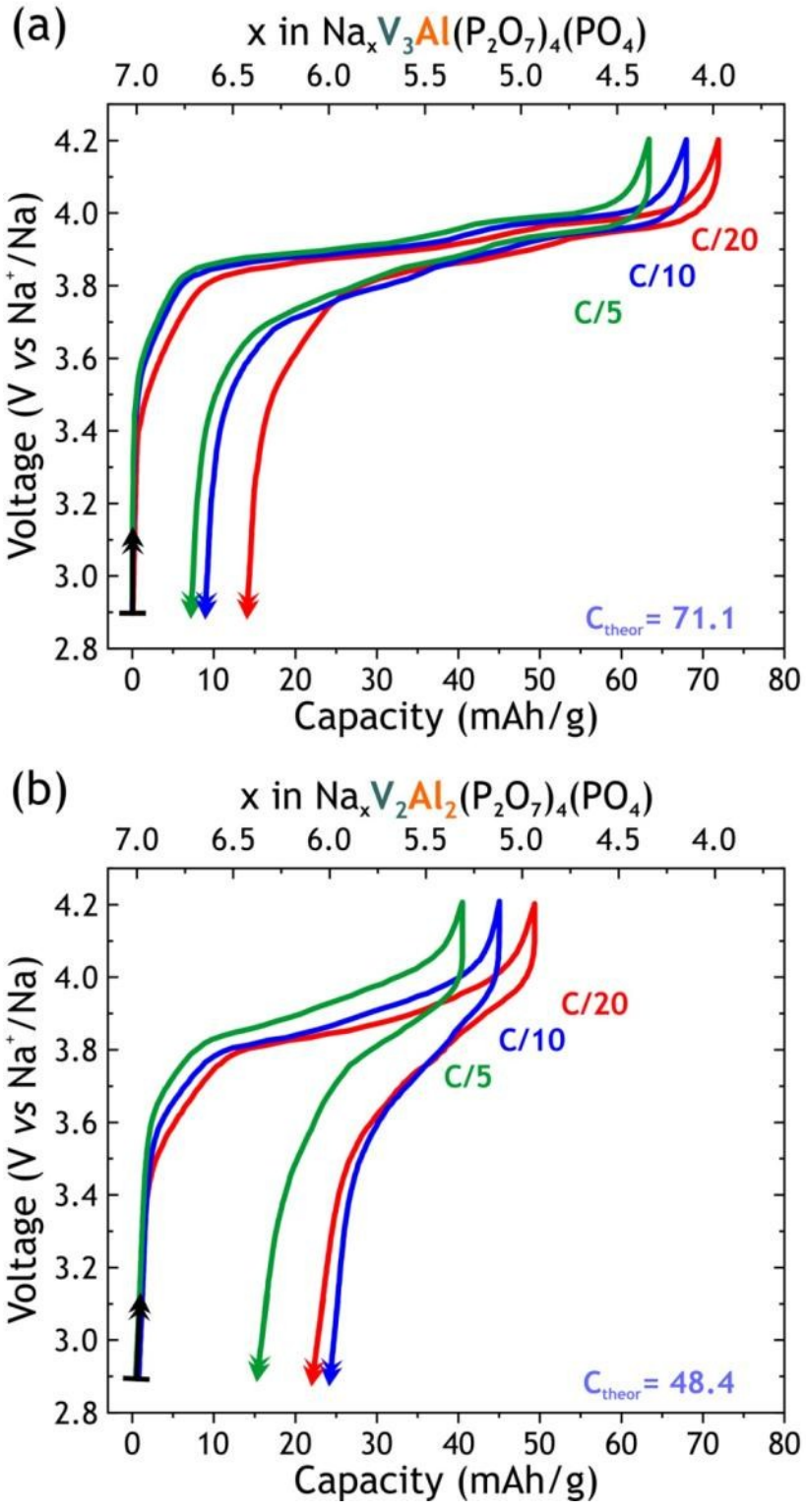

Figure S5 | First charge-discharge curves at various C rates for new $Na_7V_3Al(P_2O_7)_4(PO_4)$ (a) and $Na_7V_2Al_2(P_2O_7)_4(PO_4)$ (b) compositions cycled between 2.9 and 4.2 V *vs.* Na^+/Na.

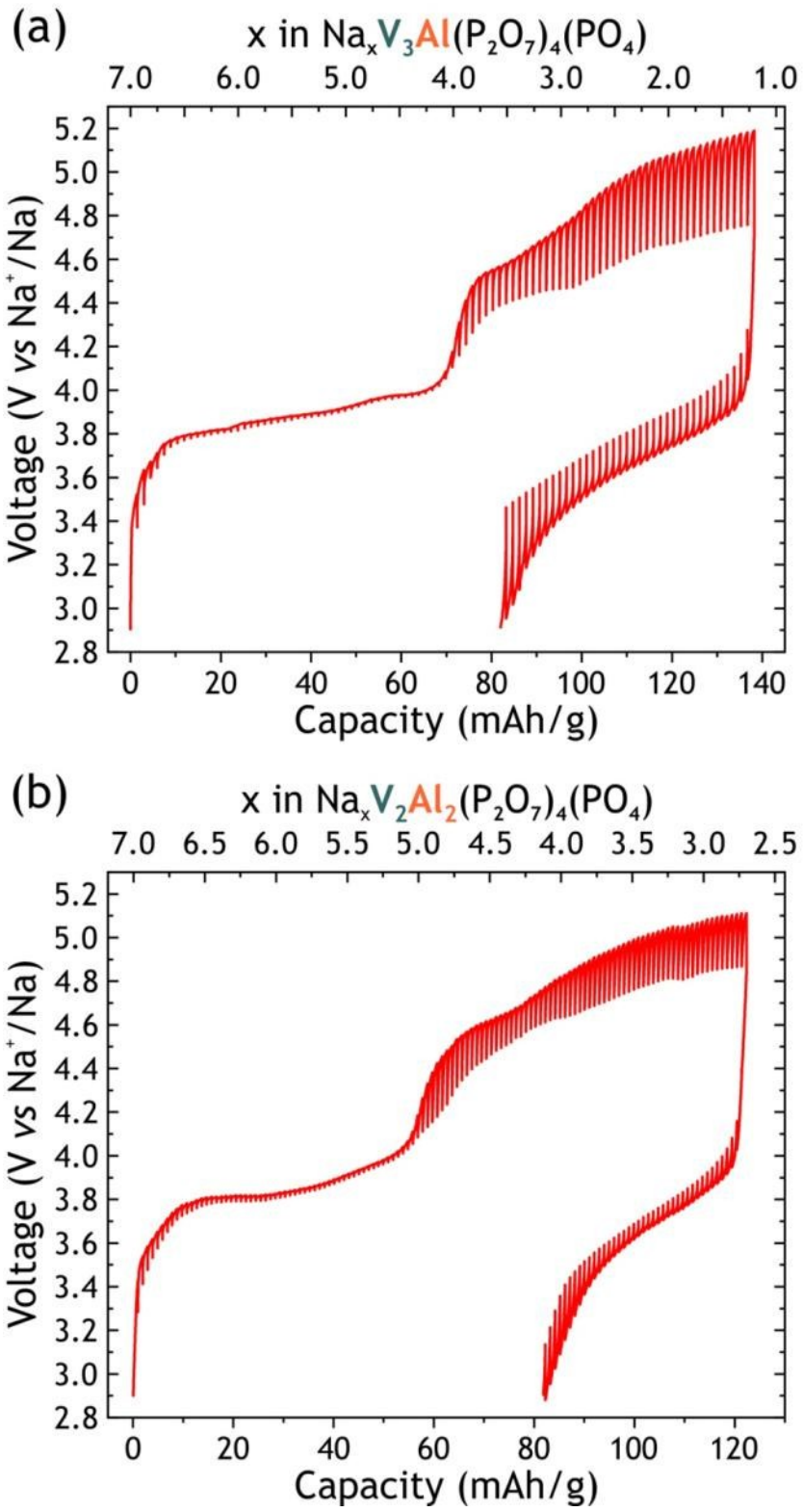

Figure S6 | GITT curves for new $Na_7V_3Al(P_2O_7)_4(PO_4)$ (a) and $Na_7V_2Al_2(P_2O_7)_4(PO_4)$ (b) compositions cycled between 2.9 and 5.0 V *vs.* Na^+/Na at C/20. GITT curves were acquired for 30 min and 1 h relaxing interval.

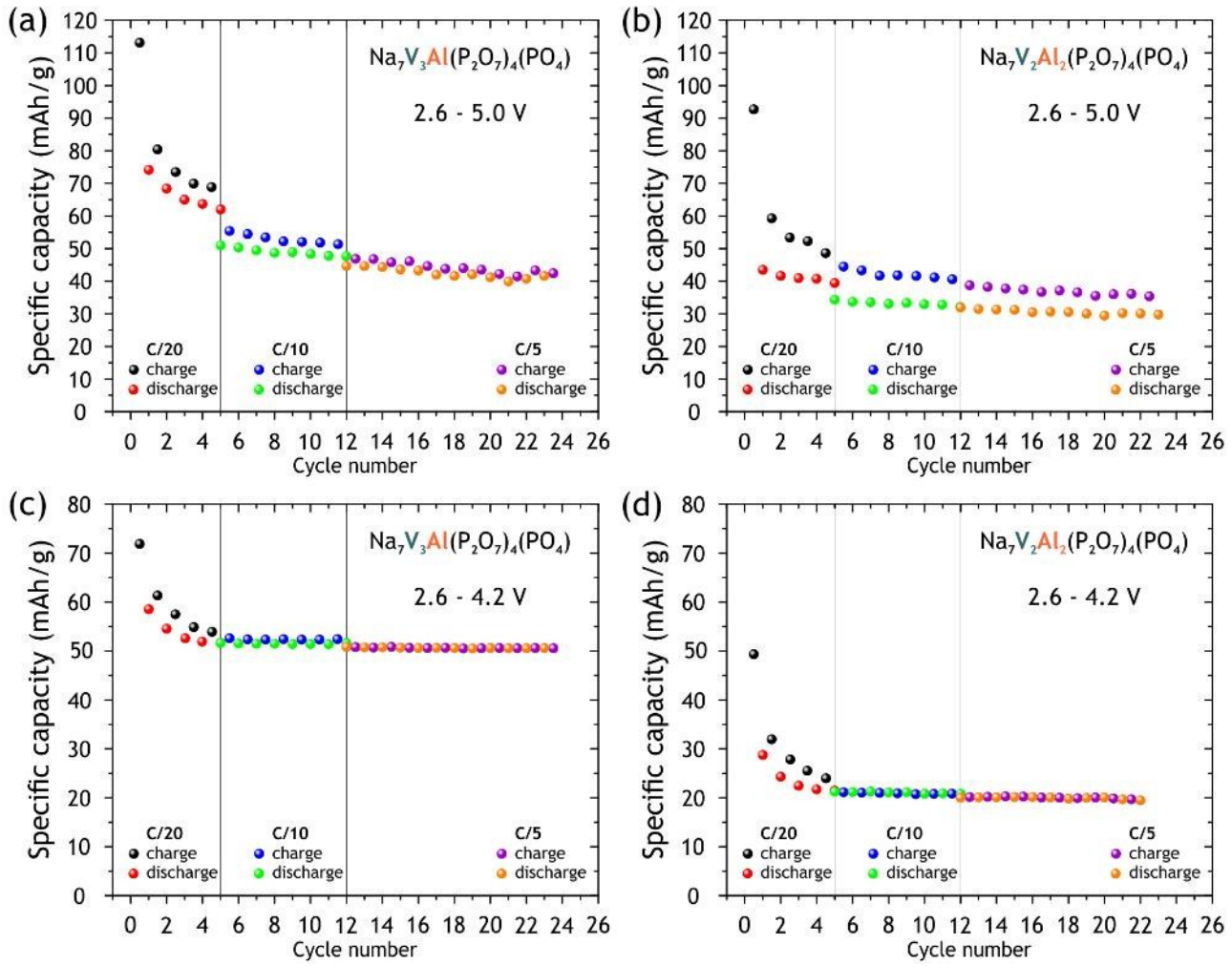

Figure S7 | Cycling performance of the $Na_7V_3Al(P_2O_7)_4(PO_4)$ (a, c) and $Na_7V_2Al_2(P_2O_7)_4(PO_4)$ (b, d) phases cycled between 2.6 and 5.0 V (a, b) and 2.6 and 4.2 V (c, d) *vs.* Na^+/Na at different current densities.

S8. In-situ XRD patterns

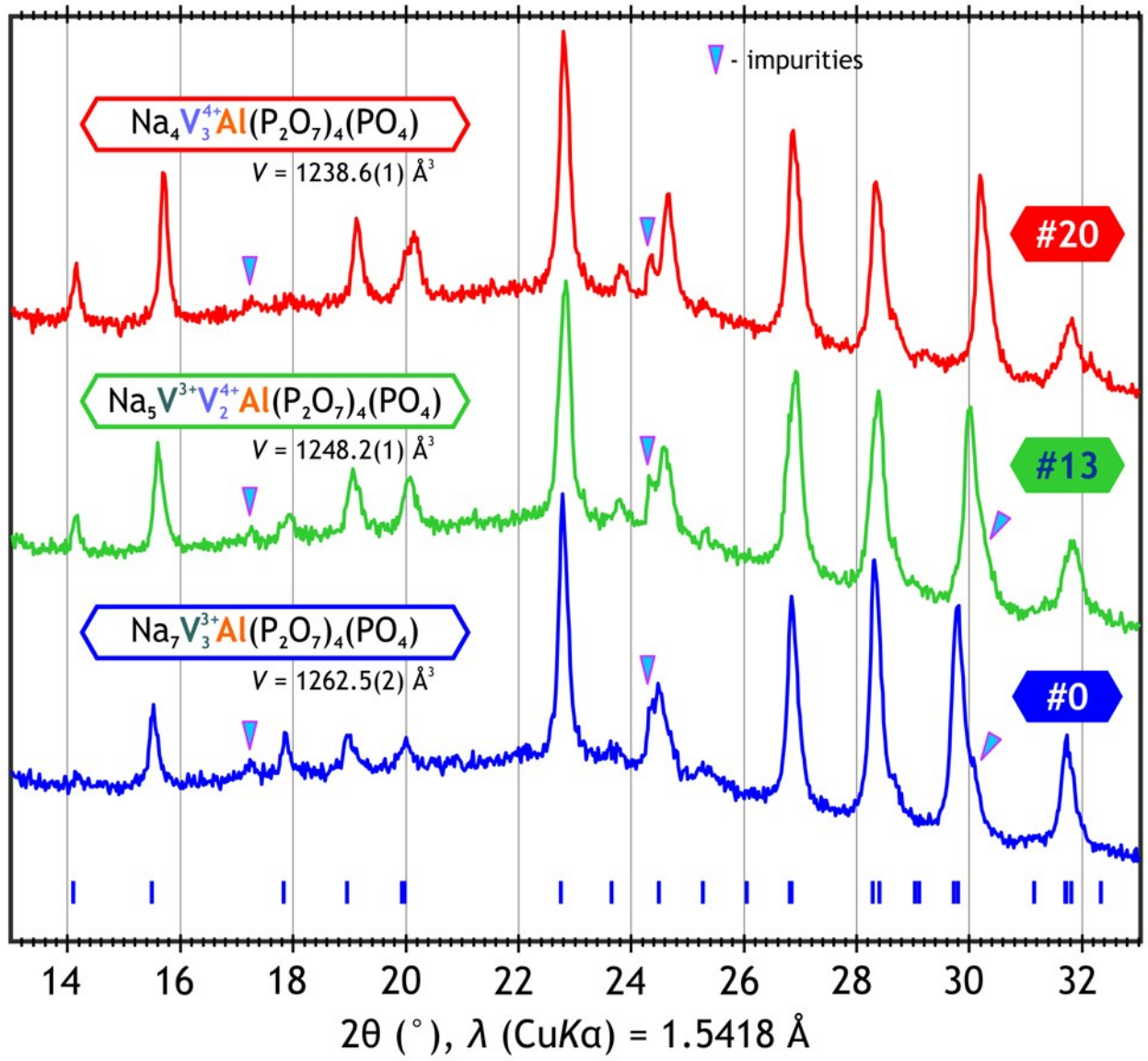

Figure S8 | *In-situ* XRD patterns of selected phases obtained upon cycling in the voltage range of 2.7–4.2 V *vs.* Na^+/Na. Reflections not associated with the studied crystal structure are indicated by blue triangles.

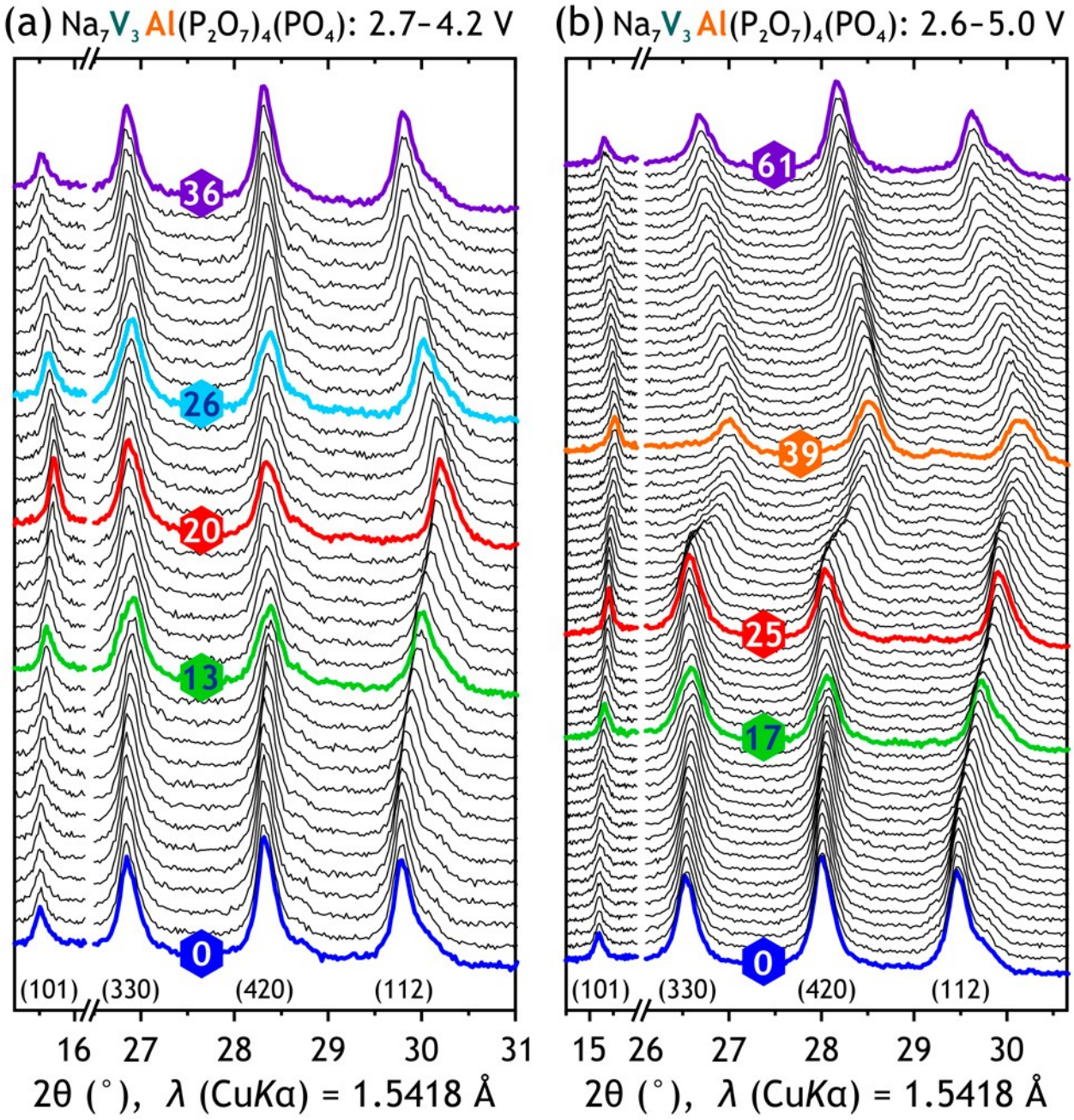

Figure S9 | Selected 2theta regions of the XRD patterns recorded *operando* for $Na_7V_3Al(P_2O_7)_4(PO_4)$ at C/20 in the 2.7–4.2 V (a) and 2.6–5.0 V (b) vs Na^+/Na voltage ranges.

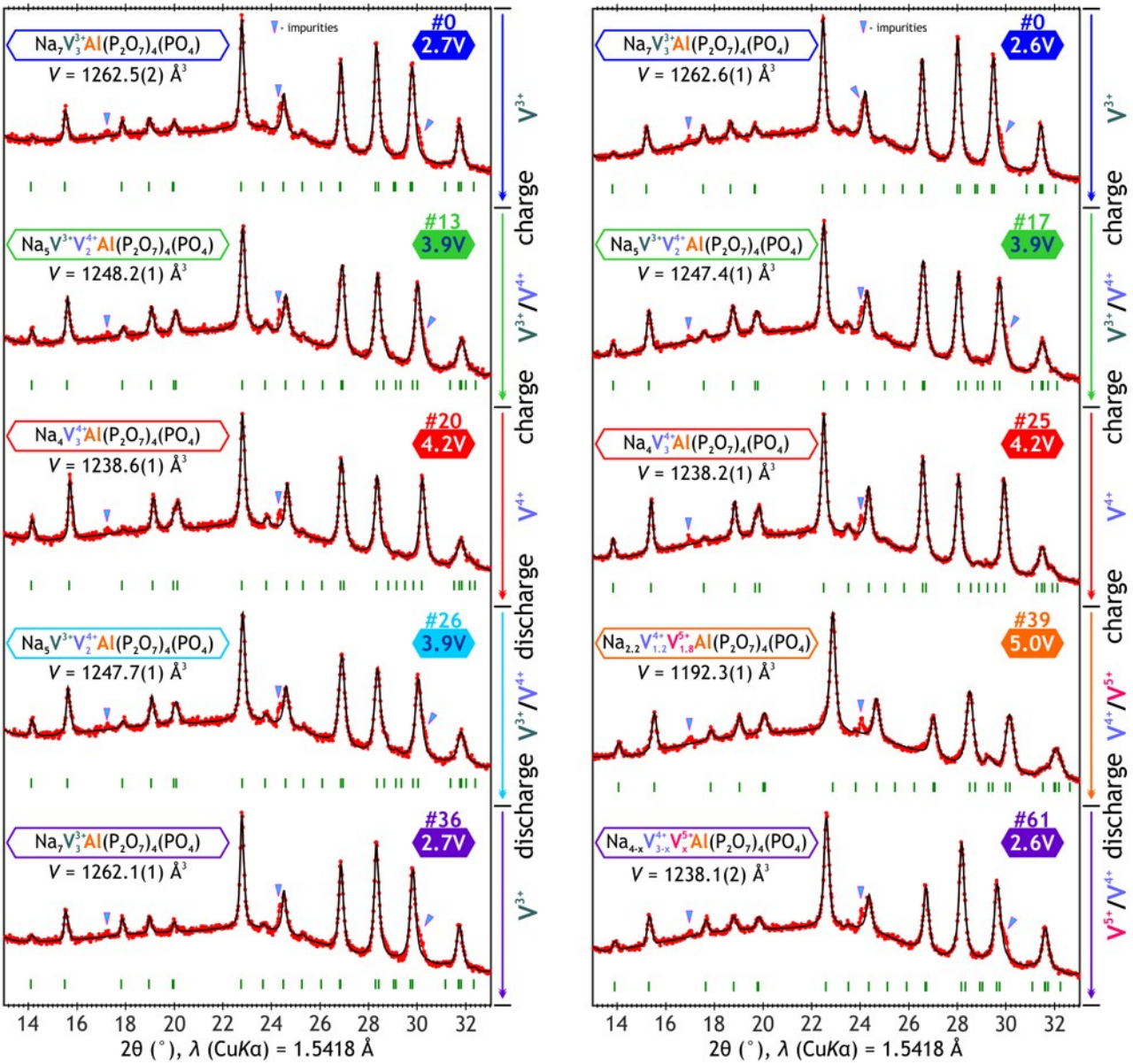

Figure S10 | *In-situ* XRD patterns of selected phases obtained upon cycling in the voltage range of 2.7–4.2 V (left) and 2.6–5.0 V (right) *vs.* Na^+/Na.