

Supplementary Information

Crystal Structure of $\text{Na}_2\text{V}_2(\text{PO}_4)_3$, an Intriguing Phase Spotted in the $\text{Na}_3\text{V}_2(\text{PO}_4)_3 - \text{Na}_1\text{V}_2(\text{PO}_4)_3$ System

Sunkyu Park ^{1,2,3}, Ziliang Wang ⁴, Zeyu Deng⁴, Iona Moog ³, Pieremanuele Canepa ^{4,5*}, François Fauth ⁶, Dany Carlier ^{2,7}, Laurence Croguennec ^{2,7}, Christian Masquelier ^{1,7} and Jean-Noël Chotard ^{1,7,*}

¹*Laboratoire de Réactivité et de Chimie des Solides, Université de Picardie Jules Verne,
CNRS-UMR 7314, F-80039 Amiens Cedex 1, France*

²*CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB UMR 5026, F-33600 Pessac, France*

³*TIAMAT, 15 Rue Baudelocque, 80000 Amiens*

⁴*Department of Materials Science and Engineering, National University of Singapore, Singapore
117575, Singapore*

⁵*Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive
4, Singapore 117585*

⁶*CELLS-ALBA Synchrotron, Cerdanya del Vallès, E-08290 Barcelona, Spain*

⁷*RS2E, Réseau Français sur le Stockage Electrochimique de l'Energie, FR CNRS 3459,
F-80039 Amiens Cedex 1, France*

Corresponding authors:

*pcanepa@nus.edu.sg

⁸jean-noel.chotard@u-picardie.fr

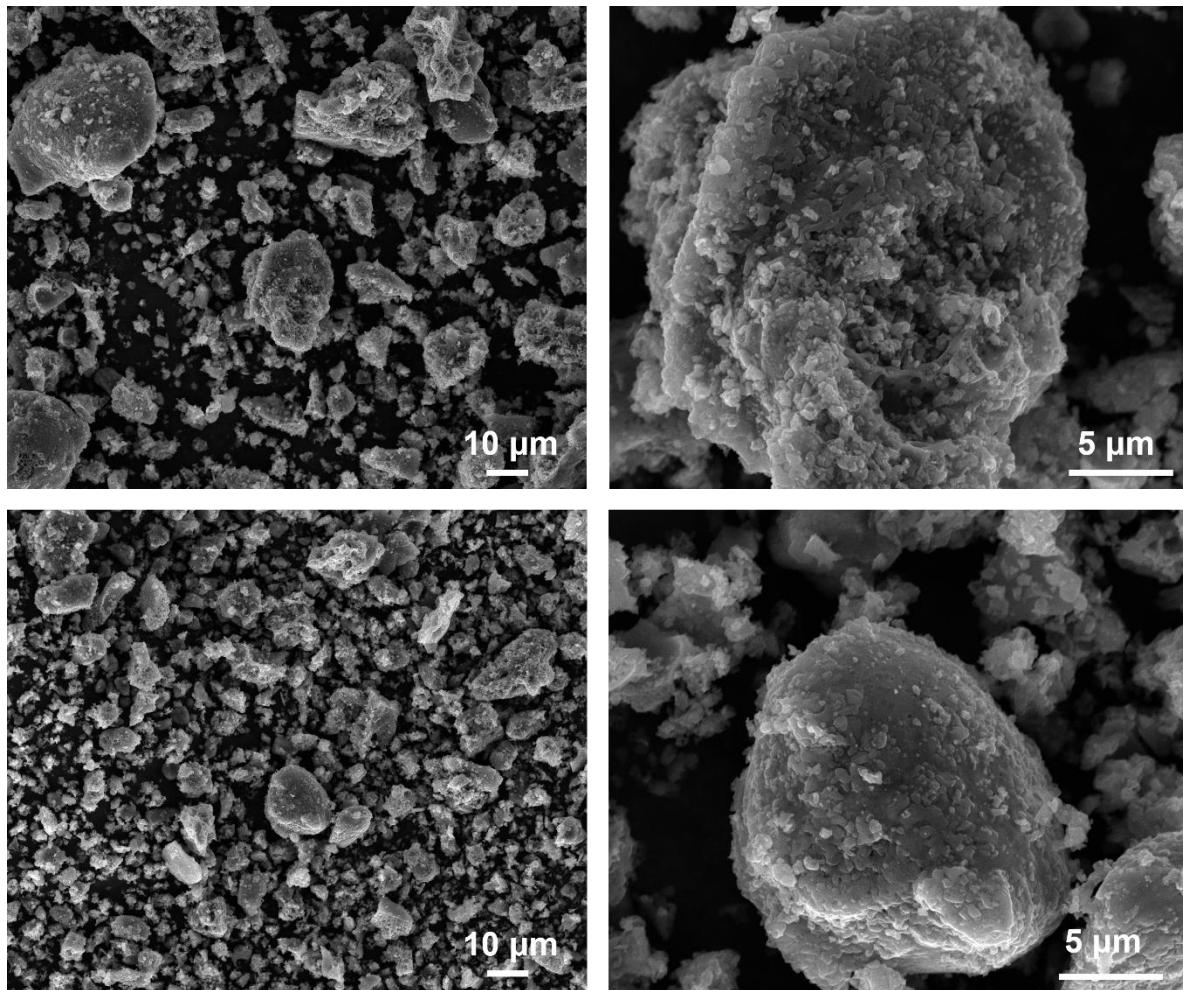


Figure S1. SEM images of the as-synthesized $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ powder.

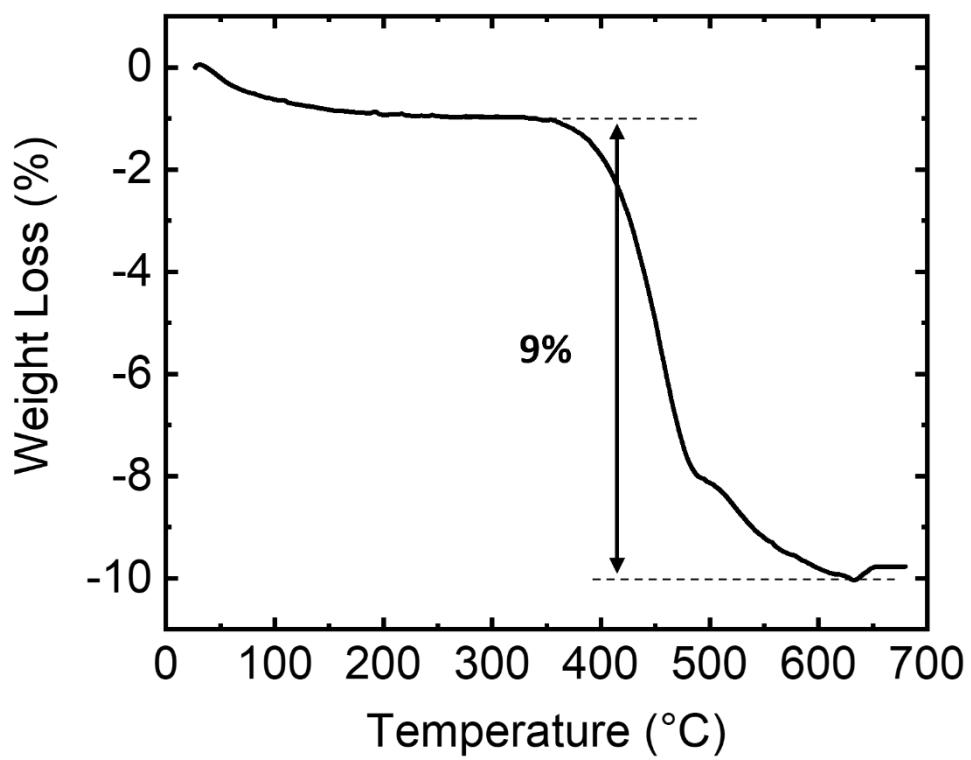


Figure S2. TGA data of the as-synthesized $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ powder.

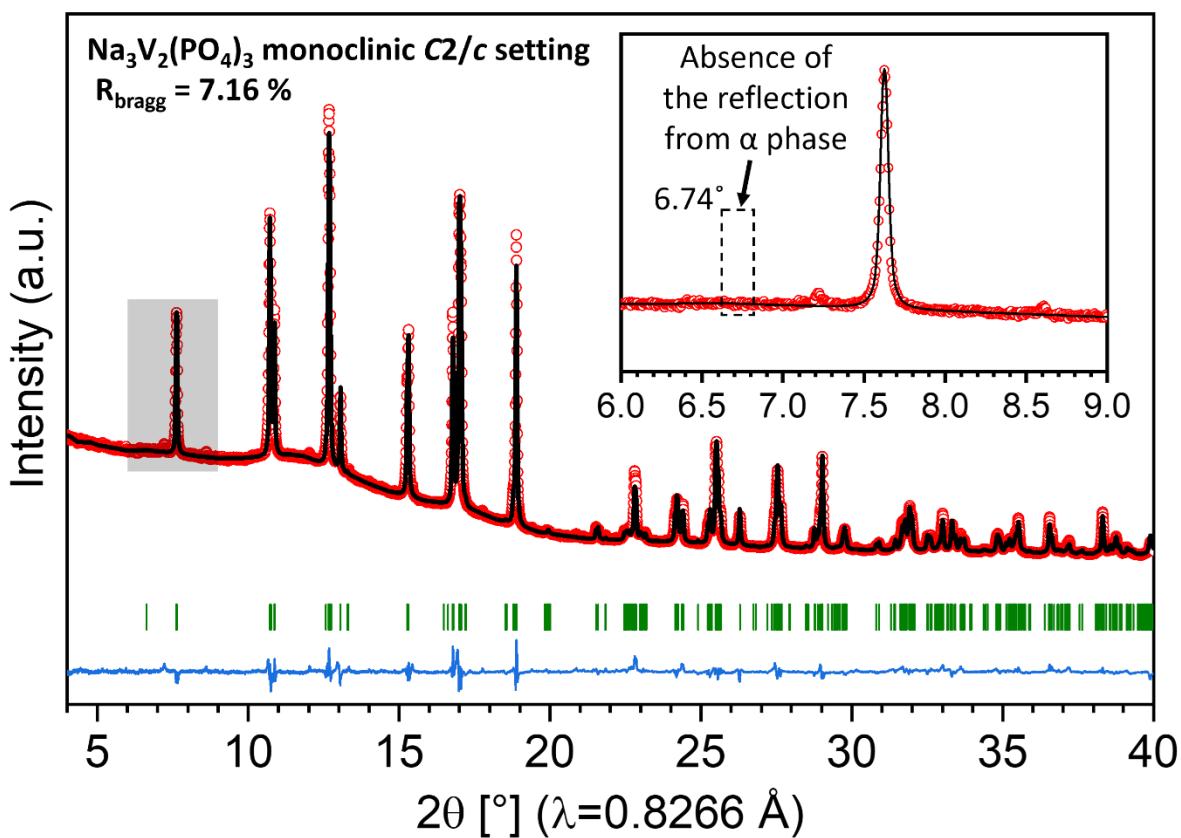


Figure S3. Rietveld refinement results of the as-synthesized $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ powder at 298 K, highlighting that the α phase structure can be excluded here as reflection at 6.74° (a clear signature from the α phase) was not observed.

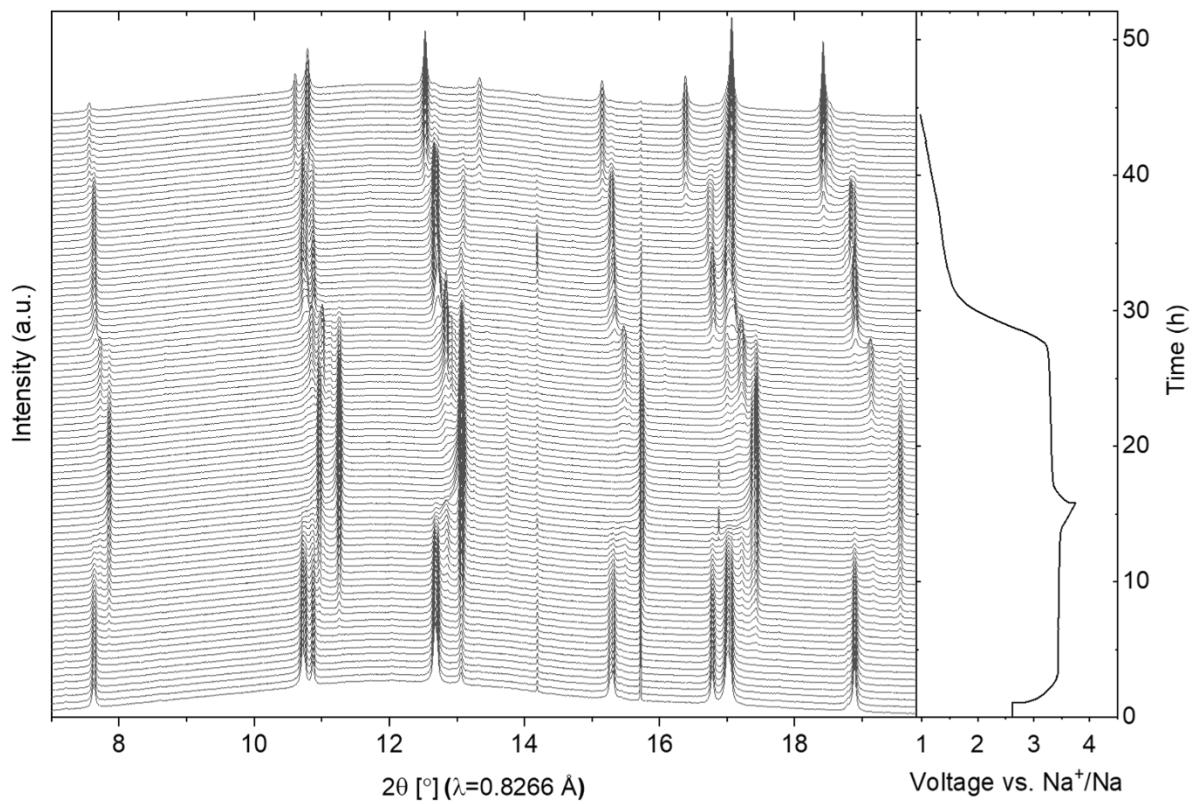


Figure S4. Wider 2θ ranged *operando* SPXRD patterns of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ during first cycle with a voltage window of 1.0 – 3.75 V vs. Na^+/Na at the C-rate of 0.11 C (=1 Na^+ in 9 h). The same data with the counter plot with the narrower 2θ range of 7.4 – 8.0° is shown in Figure 2.

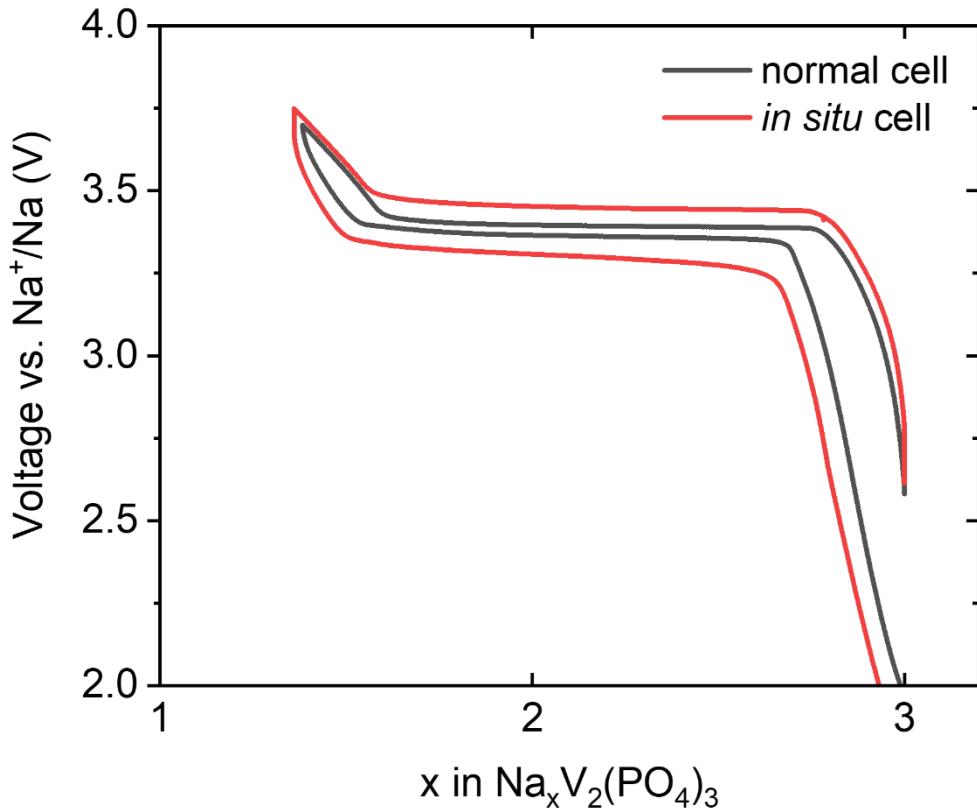


Figure S5. Comparison of a polarization between the first *in situ* cell (shown in Figure 2) and a normal coin cell cycled with the same C-rate of 0.11 C. The assembly of the normal coin cell is done with the same way as the *in situ* coin cell. The polarization of the *in situ* coin cell is about 150 mV while that of the normal coin cell is about 30 mV.

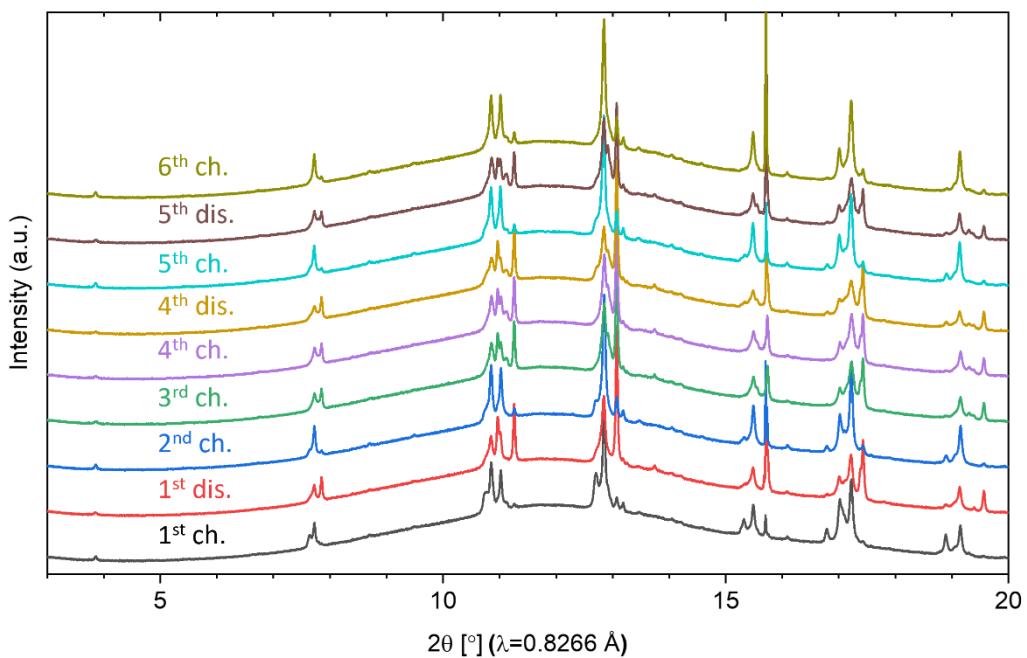
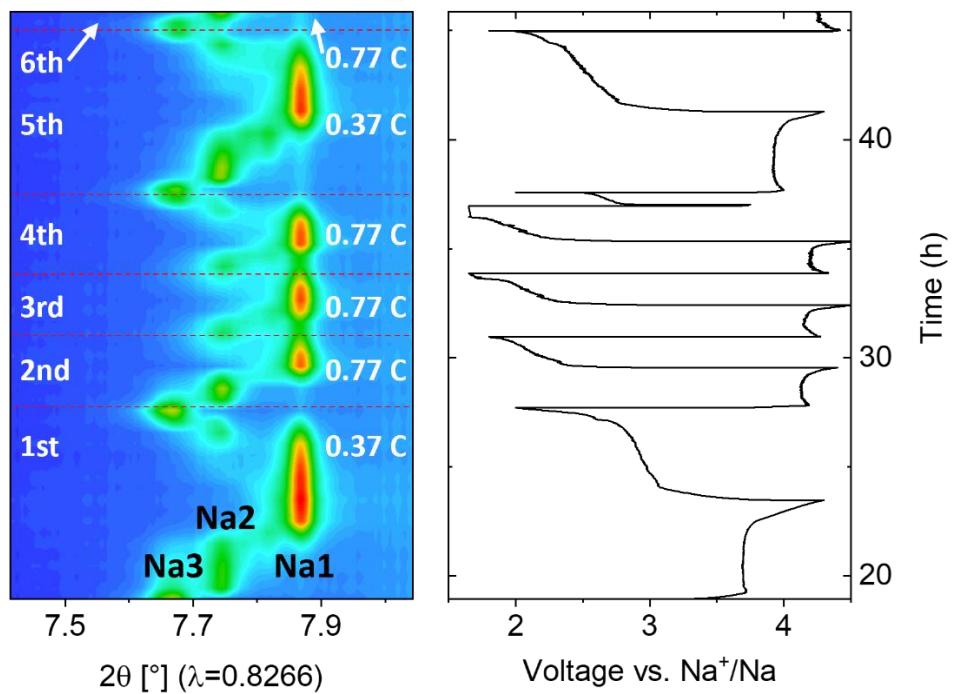


Figure S6 Top: *Operando* SPXRD measurements performed upon cycling of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as positive electrode material in a half-cell versus Na metal, during six cycles at C-rates of 0.37 or 0.77 C. The voltage windows of each cycle are given in details in Table S2. **Bottom:** the SPXRD patterns containing the most $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ phase during each cycle. Note that the $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ phase during 2nd and 3rd discharge was not observed as data point missing (fewer data points) due to higher C-rate.

Table S1. Changes in voltage windows and C-rates during *operando* XRD measurements performed upon cycling of the second cell (**Figure S5**). The measurement was stopped in the middle of charge during the sixth cycle.

Cycle number	C-rate	Lower cut-off (V)	Upper cut-off (V)
1	0.37 C	2	4.3
2	0.77 C	1.8	4.4
3	0.77 C	1.65	4.5
4	0.77 C	1.65	4.5
5	0.37 C	2	4.3
6*	0.77 C	1.65	4.5

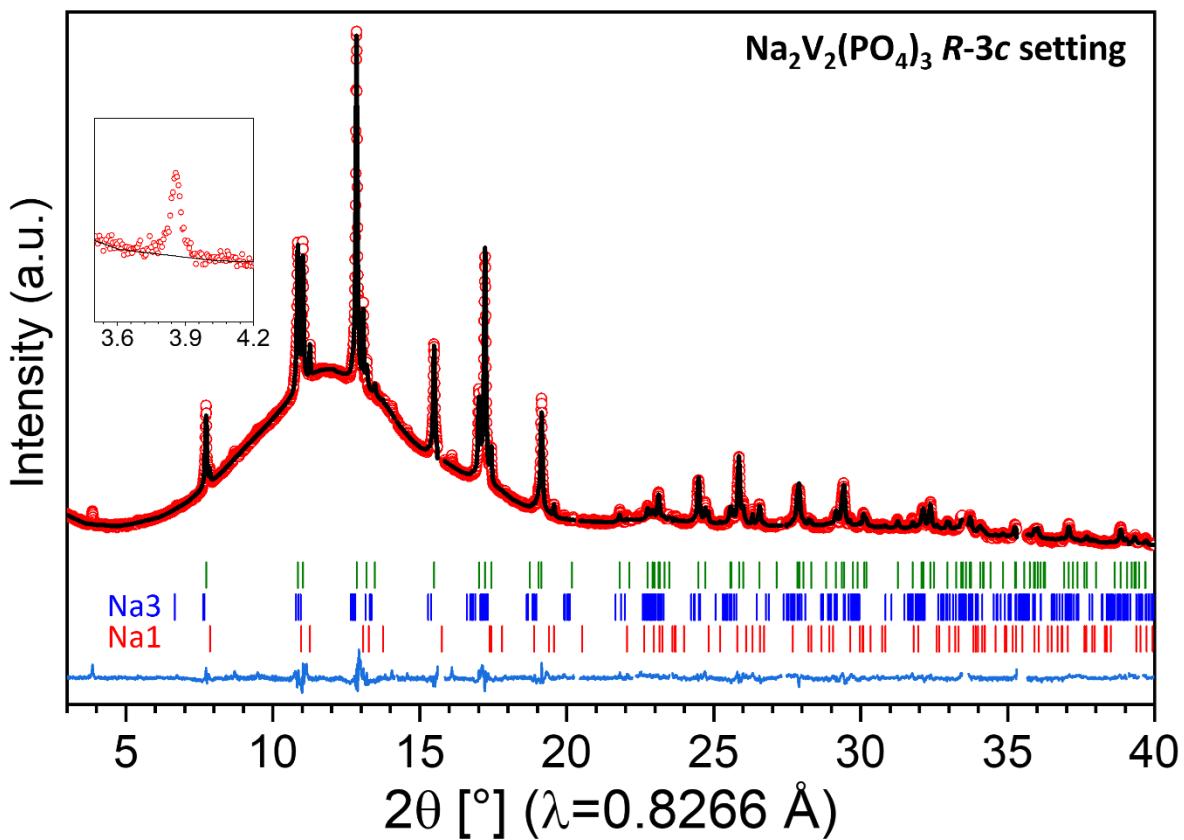


Figure S7. Rietveld refinement results of $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ with the space group $R\bar{3}c$. The reflection at 3.85° is not explained with the current structural model.

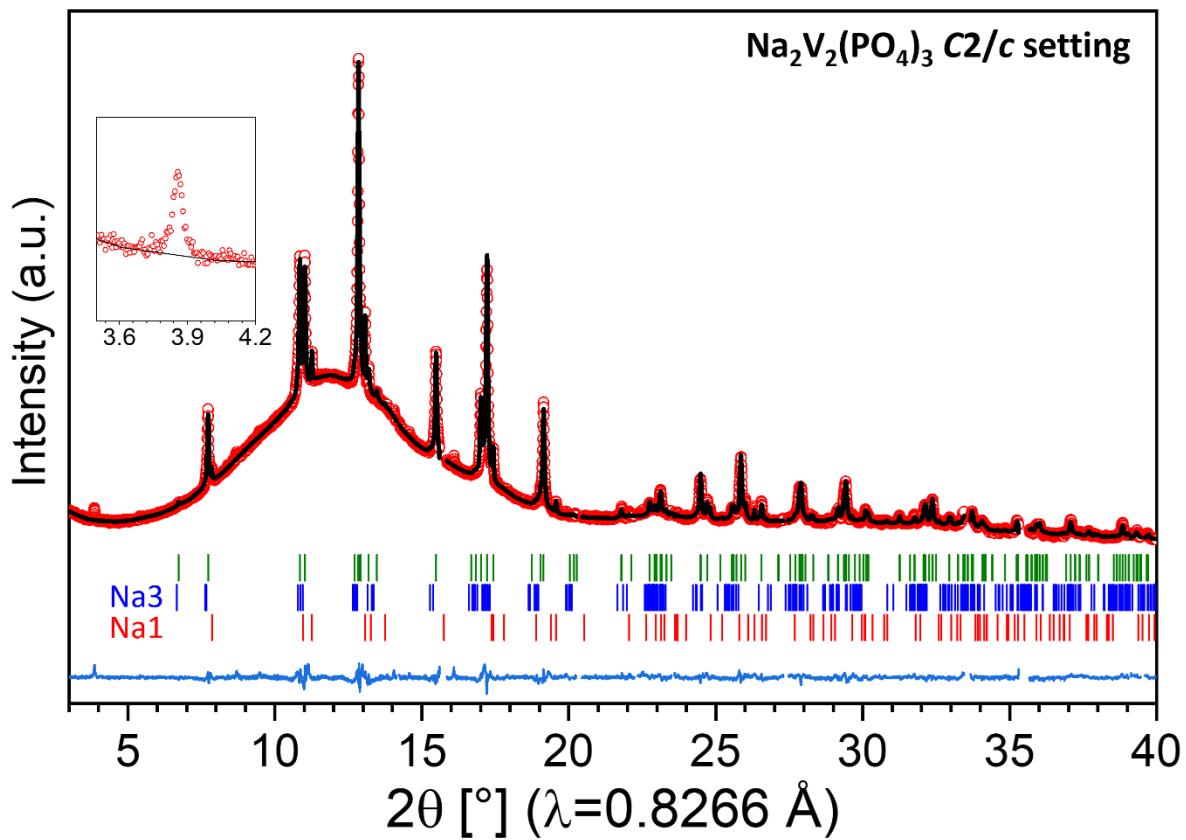


Figure S8. Rietveld refinement results of Na₂V₂(PO₄)₃ with the space group C2/c. The reflection at 3.85° is not explained with the current structural model.

Table S2. V-O bond distances obtained from Rietveld refinement of the four compositions $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ ($x = 1, 2, 3$, and 4).

$\text{Na}_4\text{V}_2(\text{PO}_4)_3$			$\text{Na}_3\text{V}_2(\text{PO}_4)_3$			$\text{Na}_2\text{V}_2(\text{PO}_4)_3$			$\text{Na}_2\text{V}_2(\text{PO}_4)_3$			$\text{Na}_1\text{V}_2(\text{PO}_4)_3$		
<i>R̄3c</i>			<i>C2/c</i>			<i>P2₁/c</i> (Model 1)			<i>P2/c</i> (Model 2)			<i>R̄3c</i>		
V(1) O(1) 2.065(14) x 3	V(1) O(1) 1.89(3)	V(1a) O(1b) 2.05(9)	V(1a) O(1b) 1.98(9)	V(1) O(1) 1.931(16) x 3										
O(2) 2.087(14) x 3	O(2) 2.00(4)	O(1d) 1.70(10)	O(1d) 1.62(9)	O(2) 1.88(2) x 3										
	O(3) 2.01(3)	O(1e) 1.93(7)	O(1e) 1.87(6)											
	O(4) 2.04(4)	O(2b) 2.17(10)	O(2b) 2.18(10)											
	O(5) 2.09(3)	O(2c) 2.03(8)	O(2c) 1.801(5)											
	O(6) 2.06(4)	O(2f) 2.06(9)	O(2f) 2.06(8)											
		avg. V(1a)-O	1.99(9)	avg. V(1a)-O	1.92(8)									
		V(1b) O(1a)	2.04(9)	V(1b) O(1a)	2.10(8)									
		O(1c) 1.85(10)		O(1c) 1.91(10)										
		O(1f) 2.17(7)		O(1f) 2.24(5)										
		O(2a) 2.01(10)		O(2a) 2.04(8)										
		O(2d) 1.82(8)		O(2d) 1.95(7)										
		O(2e) 2.08(11)		O(2e) 1.99(8)										
		avg. V(1b)-O	1.99(9)	avg. V(1b)-O	2.04(8)									
Avg.	2.076(14)		2.02(4)		1.99(9)				1.98(8)			1.91(2)		

Table S3. Refined structural parameters of the intermediate phase $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ using the space group $P2/c$ (Model 2). ^aRefined and fixed at the last stages of refinement.

$\text{Na}_2\text{V}_2(\text{PO}_4)_3$						
Space group: $P2/c$ (#13); $Z = 4$						
$a = 15.2380(5)$ Å; $b = 8.6090(5)$ Å; $c = 8.7390(4)$; $\beta = 126.289(5)$						
$V = 924.05(7)$ Å ³ ; $V/Z = 231.01(2)$ Å ³						
$R_{wp} = 12.8\%$; $R_p = 18.0\%$; $R_{\text{bragg}} = 7.50\%$						
Atom	Wyckoff position	x/a	y/b	z/c	Uiso, Å ²	Occ.
V(1a)	4g	0.600(2)	0.243(4)	0.649(4)	0.026(3)	1
V(1b)	4g	0.108(2)	0.741(4)	0.645(4)	0.026(3)	1
P(1a)	4g	0.8498(10)	0.113(2)	0.932(2)	0.029(3)	1
P(1b)	4g	0.3569(10)	0.605(2)	0.958(2)	0.029(3)	1
P(2a)	2e	0	0.534(2)	0.25	0.029(3)	1
P(2b)	2f	0.5	0.021(2)	0.25	0.029(3)	1
O(1a)	4g	0.143(6)	0.149(10)	0.389(7)	0.012(3)	1
O(1b)	4g	0.660(7)	0.643(10)	0.389(10)	0.012(3)	1
O(2a)	4g	0.072(6)	0.451(10)	0.204(10)	0.012(3)	1
O(2b)	4g	0.553(6)	0.888(5)	0.214(10)	0.012(3)	1
O(3a)	4g	0.458(4)	0.678(10)	0.990(10)	0.012(3)	1
O(3b)	4g	0.937(4)	0.184(7)	0.919(10)	0.012(3)	1
O(4a)	4g	0.157(7)	0.064(2)	0.082(10)	0.012(3)	1
O(4b)	4g	0.635(7)	0.573(2)	0.020(4)	0.012(3)	1
O(5a)	4g	0.734(3)	0.840(10)	0.265(7)	0.012(3)	1
O(5b)	4g	0.259(5)	0.325(10)	0.273(7)	0.012(3)	1
O(6a)	4g	0.085(6)	0.364(10)	0.920(7)	0.012(3)	1
O(6b)	4g	0.581(6)	0.882(10)	0.929(7)	0.012(3)	1
Na(1)	4g	0.275(4)	0.280(7)	0.050(7)	0.030(13)	0.98(3)
Na(2a ₁)	4g	0.695 ^a	0.937 ^a	0.603 ^a	0.030(13)	0.17(7)
Na(2a ₂)	4g	0.172 ^a	0.446 ^a	0.570 ^a	0.030(13)	0.21(7)
Na(2b ₁)	2e	0	0.916(10)	0.25	0.030(13)	0.63(11)
Na(2b ₂)	2f	0.5	0.362(13)	0.25	0.030(13)	0.68(11)

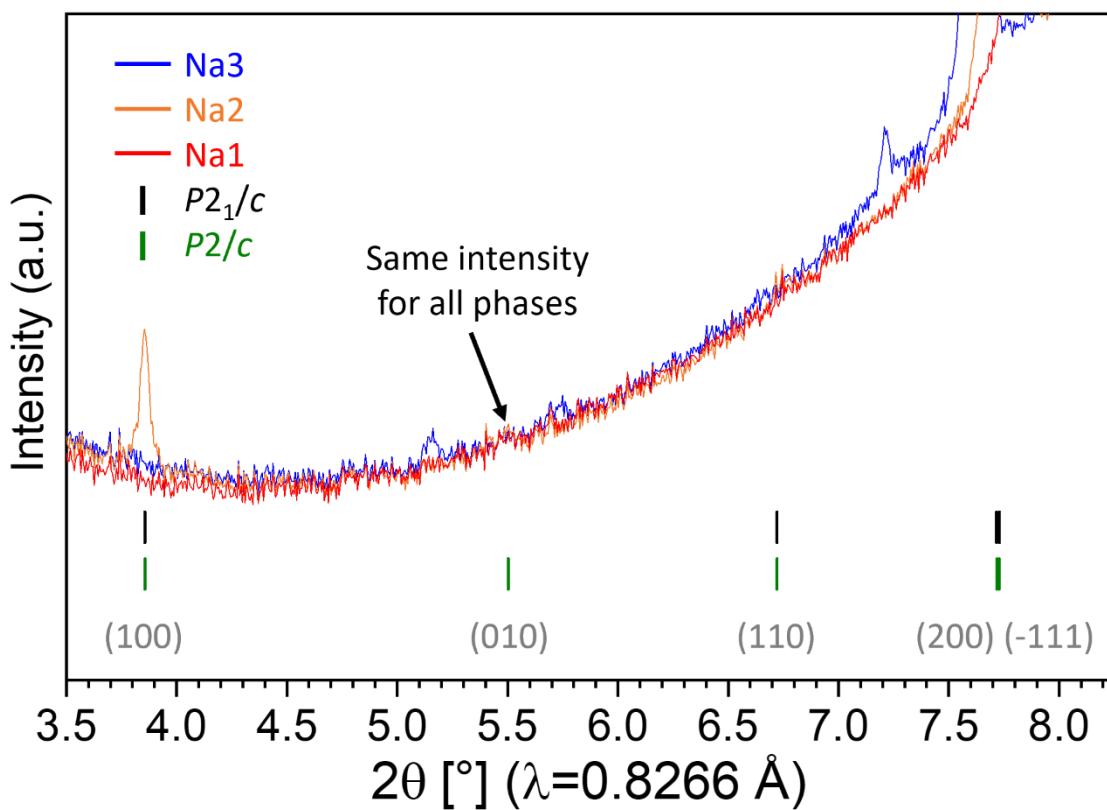


Figure S9. Comparison of the space group $P2_1/c$ and $P2/c$ for the structural determination of $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ phase. The same intensity for the possible (010) reflection (from the $P2/c$ structural model) was observed in the XRD patterns of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_2\text{V}_2(\text{PO}_4)_3$, and $\text{Na}_1\text{V}_2(\text{PO}_4)_3$, suggesting it is not a peak but noisy background.

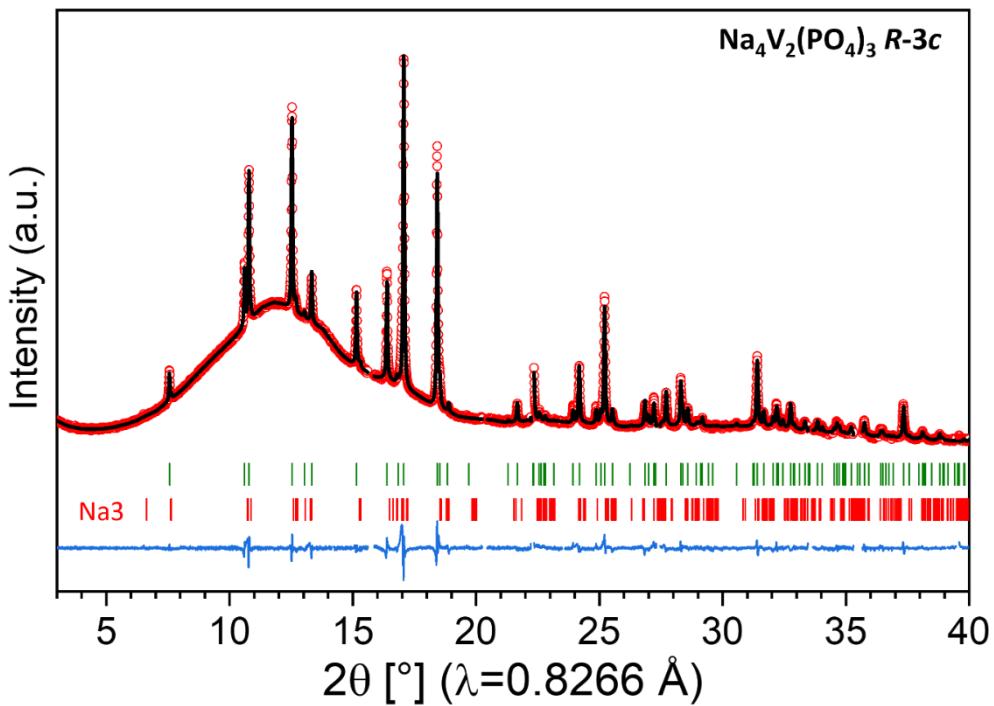


Figure S10. Rietveld refinement results of $\text{Na}_4\text{V}_2(\text{PO}_4)_3$. The XRD pattern was obtained from *operando* measurements. The contributions from Na metal and Al foil are removed

Table S4. Refined structural parameters of the $\text{Na}_4\text{V}_2(\text{PO}_4)_3$ using the space group $R\bar{3}c$.

$\text{Na}_4\text{V}_2(\text{PO}_4)_3$
 Space group: $R\bar{3}c$ (#167); $Z = 6$
 $a = 8.94302(10)$ Å; $c = 21.3609(4)$ Å; $c/a = 2.389$
 $V = 1479.51(4)$ Å³; $V/Z = 246.585(7)$ Å³
 $R_{wp} = 14.1\%$; $R_p = 19.5\%$; $R_{\text{bragg}} = 4.2\%$

Atom	Wyckoff position	x/a	y/b	z/c	Uiso, Å ²	Occ.
V(1)	12c	0	0	0.1467(3)	0.014(2)	1
P(1)	18e	0.2970(11)	0	0.25	0.021(4)	1
Na(1)	6b	0	0	0	0.031(9)	0.97(4)
Na(2)	18e	0.6461(14)	0	0.25	0.021(8)	0.92(2)
O(1)	36f	0.013(2)	0.2099(14)	0.1921(5)	0.020(5)	1
O(2)	36f	0.1827(14)	0.1713(14)	0.0833(7)	0.024(4)	1

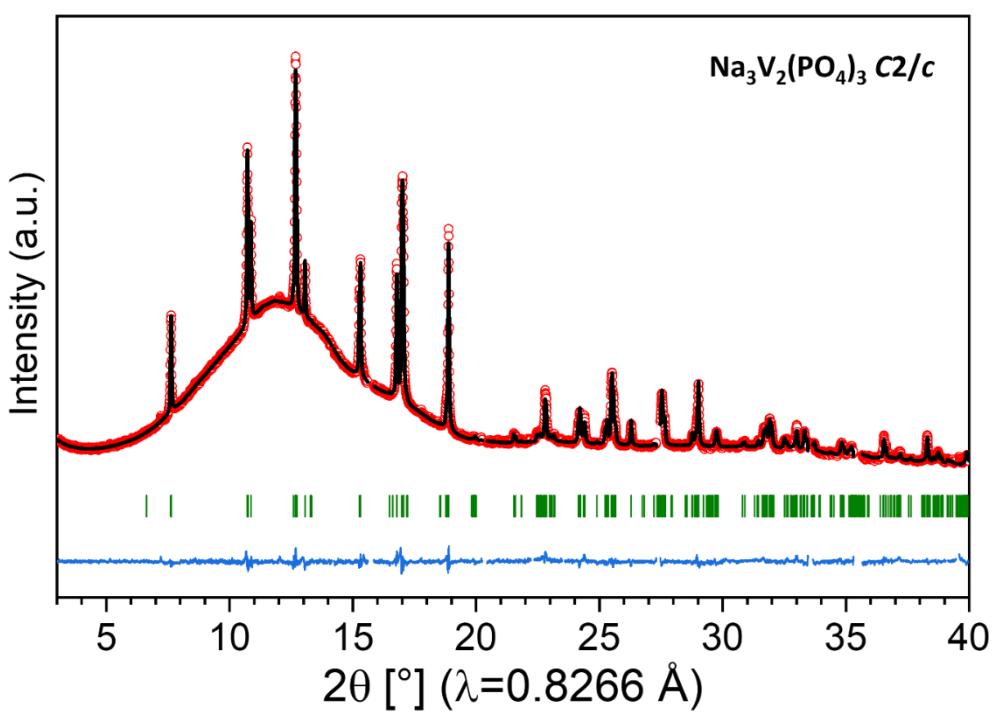


Figure S11. Rietveld refinement results of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. The XRD pattern was obtained from *operando* measurements. The contributions from Na metal and Al foil are removed

Table S5. Refined structural parameters of the intermediate phase $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ using the space group $C2/c$. The XRD pattern was obtained from *operando* measurements.

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$						
Space group: $C2/c$ (#15); $Z = 4$						
$a = 15.4065(3) \text{ \AA}$; $b = 8.7288(2) \text{ \AA}$; $c = 8.8243(2)$; $\beta = 126.1091(16)$						
$V = 958.73(4) \text{ \AA}^3$; $V/Z = 239.682(10) \text{ \AA}^3$						
$R_{wp} = 11.2 \%$; $R_p = 17.5 \%$; $R_{\text{bragg}} = 7.17 \%$						
Atom	Wyckoff position	x/a	y/b	z/c	Uiso, \AA^2	Occ.
V(1)	8f	0.6029(6)	0.253(3)	0.6500(14)	0.015(2)	1
P(1)	8f	0.8514(11)	0.0999(14)	0.9620(14)	0.021(3)	1
P(2)	4e	0	0.532(2)	0.25	0.021(3)	1
O(1)	8f	0.138(2)	0.126(4)	0.357(3)	0.011(2)	1
O(2)	8f	0.0763(18)	0.450(3)	0.221(3)	0.011(2)	1
O(3)	8f	0.4510(18)	0.670(3)	0.987(4)	0.011(2)	1
O(4)	8f	0.156(2)	0.076(2)	0.066(4)	0.011(2)	1
O(5)	8f	0.7587(18)	0.828(4)	0.275(3)	0.011(2)	1
O(6)	8f	0.073(2)	0.361(3)	0.919(3)	0.011(2)	1
Na(1)	4c	0.25	0.25	0	0.059(9)	0.679(14)
Na(2a)	8f	0.665(2)	0.927(5)	0.634(5)	0.059(9)	0.70(3)
Na(2b)	4e	0	0.877(6)	0.25	0.059(9)	0.87(2)

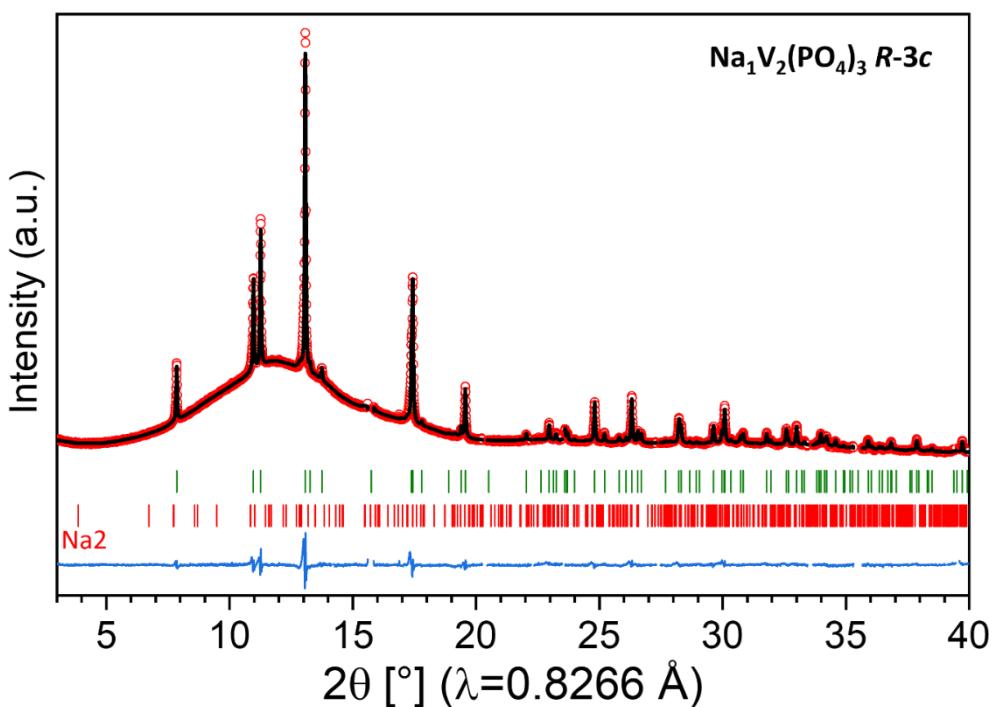


Figure S12. Rietveld refinement results of $\text{Na}_1\text{V}_2(\text{PO}_4)_3$. The XRD pattern was obtained from *operando* measurements. The contributions from Na metal and Al foil are removed.

Table S6. Refined structural parameters of the $\text{Na}_4\text{V}_2(\text{PO}_4)_3$ using the space group $R\bar{3}c$.

$\text{Na}_1\text{V}_2(\text{PO}_4)_3$
 Space group: $R\bar{3}c$ (#167); $Z = 6$
 $a = 8.42631(12)$ Å; $c = 21.4772(6)$ Å; $c/a = 2.549$
 $V = 1320.63(5)$ Å³; $V/Z = 220.105(8)$ Å³
 $R_{wp} = 15.8\%$; $R_p = 24.3\%$; $R_{\text{Bragg}} = 7.69\%$

Atom	Wyckoff position	x/a	y/b	z/c	Uiso, Å ²	Occ.
V(1)	12c	0	0	0.1450(4)	0.024(3)	1
P(1)	18e	0.285(1)	0	0.25	0.023(4)	1
Na(1)	6b	0	0	0	0.034(0)	0.96(4)
O(1)	36f	0.187(2)	0.160(2)	0.087(1)	0.017(5)	1
O(2)	36f	0.023(3)	0.198(2)	0.192(1)	0.014(5)	1