Soft-Chemical Scalable One-pot Aqueous-medium Synthesis of $Na_3(VO)_2(PO_4)_2F$-Based Cathodes: Compositional Tuning and Electrochemical Performance in Na- and Li-Ion Batteries

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Solution preparation for ICP-OES and Ion-chromatographic analysis

ICP analysis for Na was performed on Perkin Elmer AVIO 200 ICP-OES. The samples, **I-IV** were digested overnight in hydrothermal bombs in 1% ultra-high pure ICP grade HNO_3. The sample solution was then diluted to 15 ppm strength for the measurements. The standard solution for Na was tested at various strengths, 0.1 0.5, 1, 5 and 10 ppm, before performing the analysis for samples.

Ion Chromatography for the analysis of fluoride was carried out in a Thermofisher INUVION - Ion Chromatography. The samples digested in 1% ICP grade HNO_3. Then the solution was diluted to 15 ppm using Milli-Q water for the analysis. The instrument was calibrated at various low concentrations (0.3125, 0.625, 1.25, 2.5, 5 and 10 ppm) of known fluoride standard solutions.

Post-mortem XRD analysis of the Na- and Li-ion cells

Na- and Li-ion coin cells were disassembled inside the Ar-filled glovebox after they have been charged or discharged to the designated potential. The cathode composite was then washed with acetonitrile and dried in vacuum in the antechamber. The dried cathode composite was then loaded on a air-tight cell for laboratory powder X-ray diffraction.

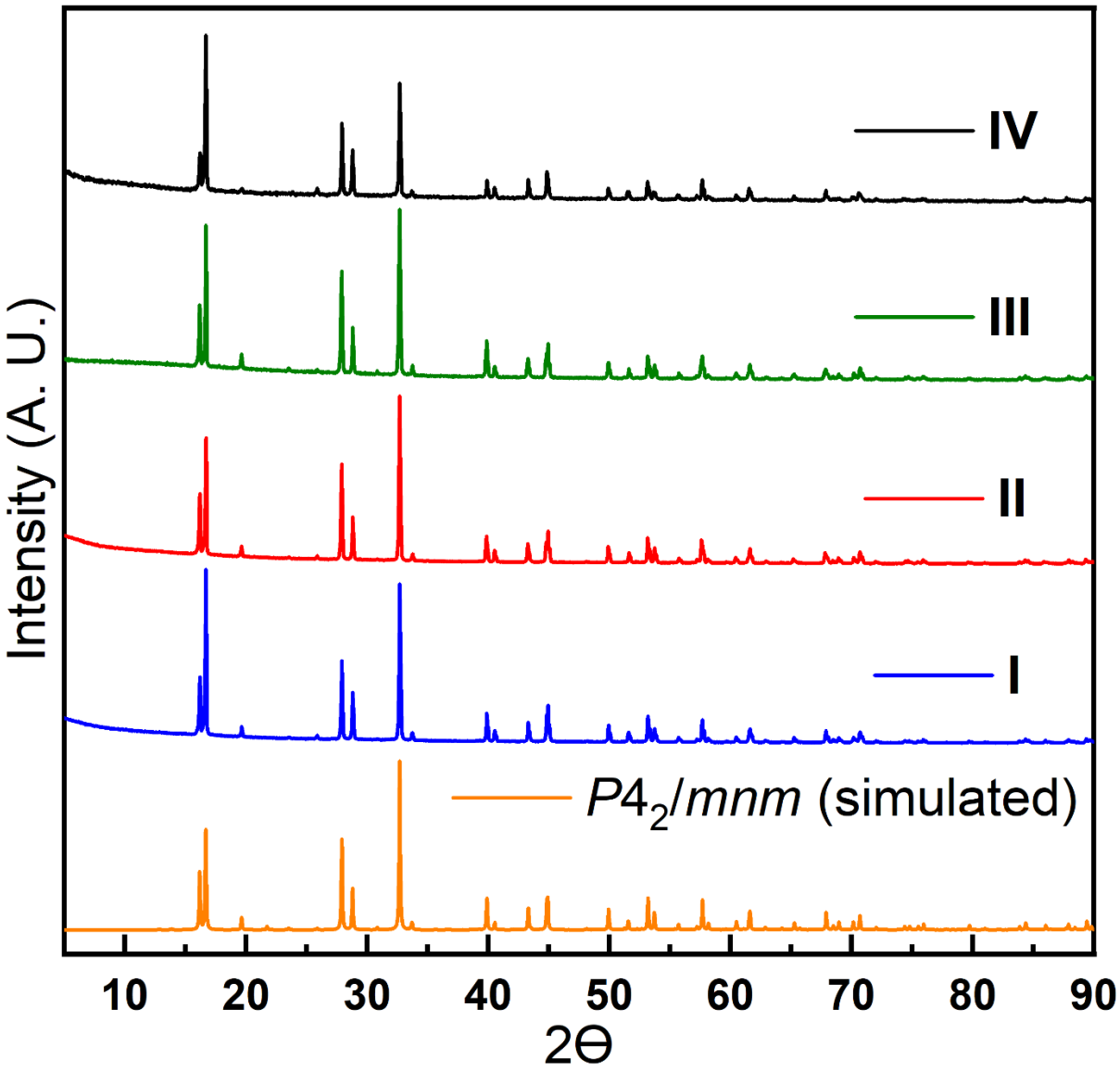

Fig. S1. The laboratory PXRD (Cu $K_{\alpha1,2}$ (λ) = 1.54059 Å) of **I** – **IV**, plotted over the simulated pattern of **I** solved in *P*4$_2$/*mnm* space group. The stack plot shows very good matching of the experimental patterns with theoretical pattern indicating purity of bulk phase.

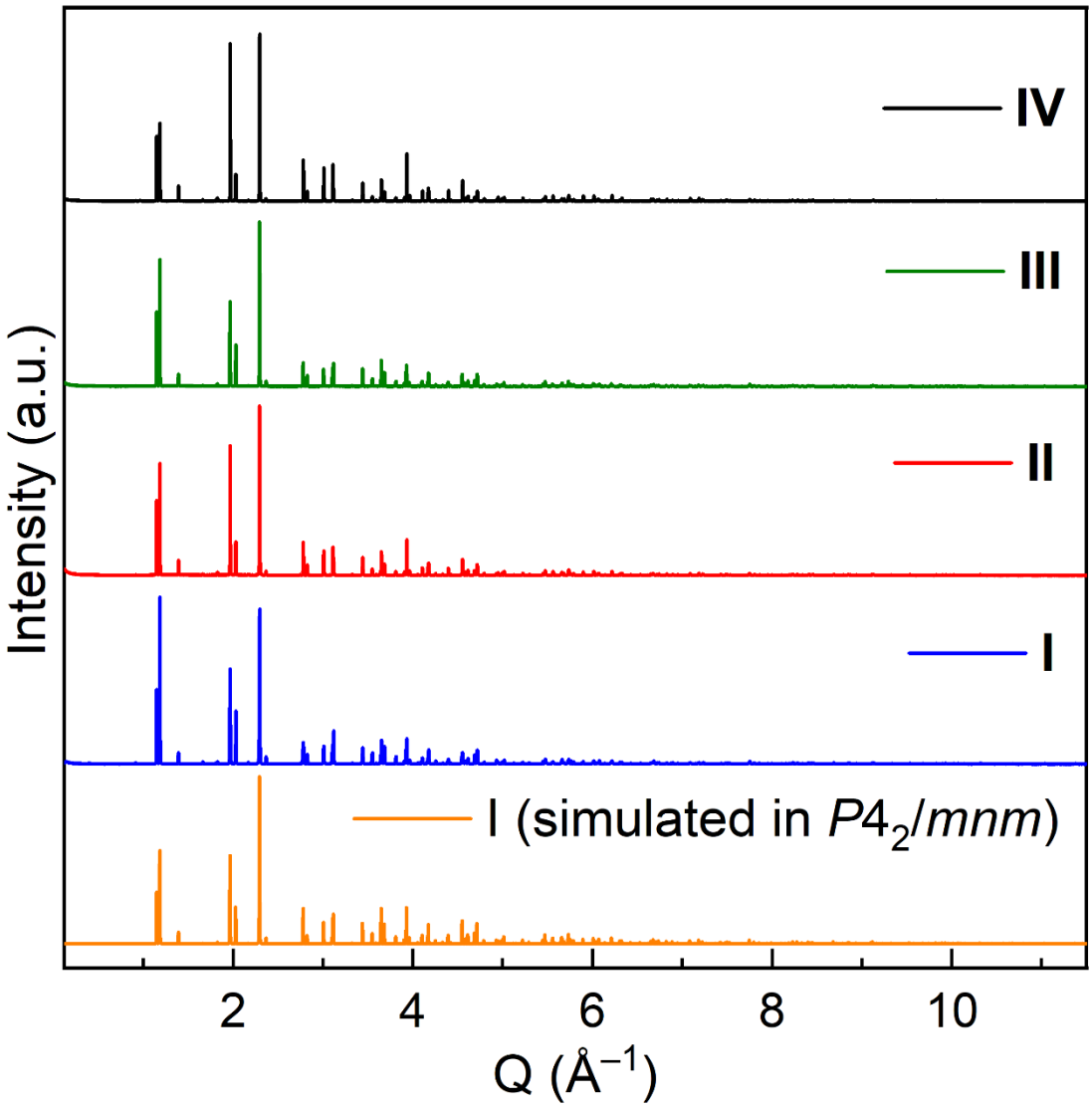

Fig. S2. The synchrotron PXRD (λ = 0.457902 Å for **I,** 0.457867 Å for **II,** 0.459727 Å for **III**, 0.412834 Å for **IV**) of **I** – **IV**, plotted in terms of *Q* space (Å^{-1}) showing excellent matching with the simulated pattern of **I** in $P4_2/mnm$ space group. Absence of any additional line proves the bulk purity of the products.

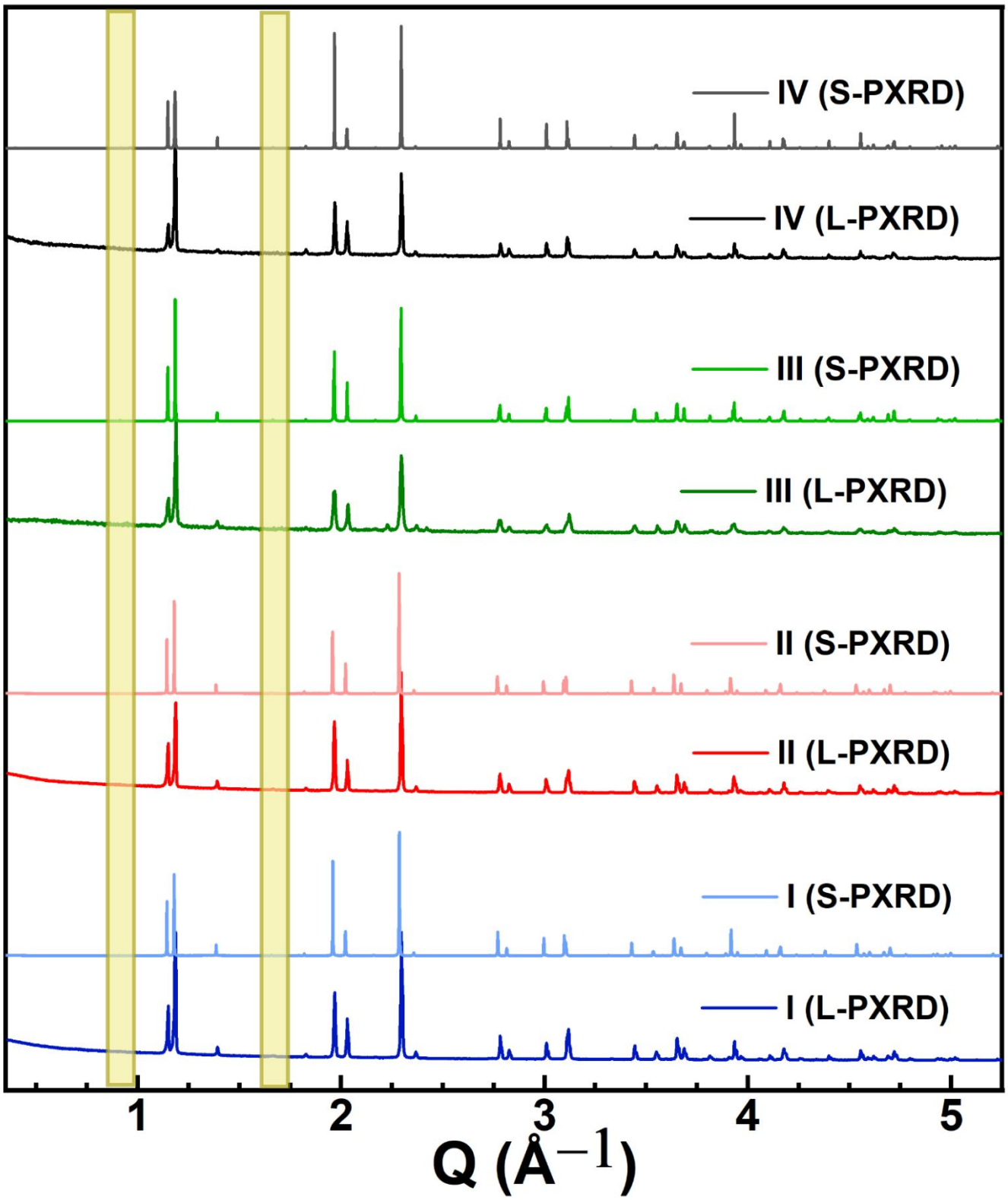

Fig. S3. A one-to-one comparison of the synchrotron (λ ~ 0.4578Å) and laboratory PXRD ($\lambda_{Cu\ K\alpha1,2}$ = 1.54059 Å) of **I** – **IV**, plotted in terms of *Q* vector (Å^{-1}) for consistency. The highlighted sections are zoomed in in Figure S4 to show the difference.

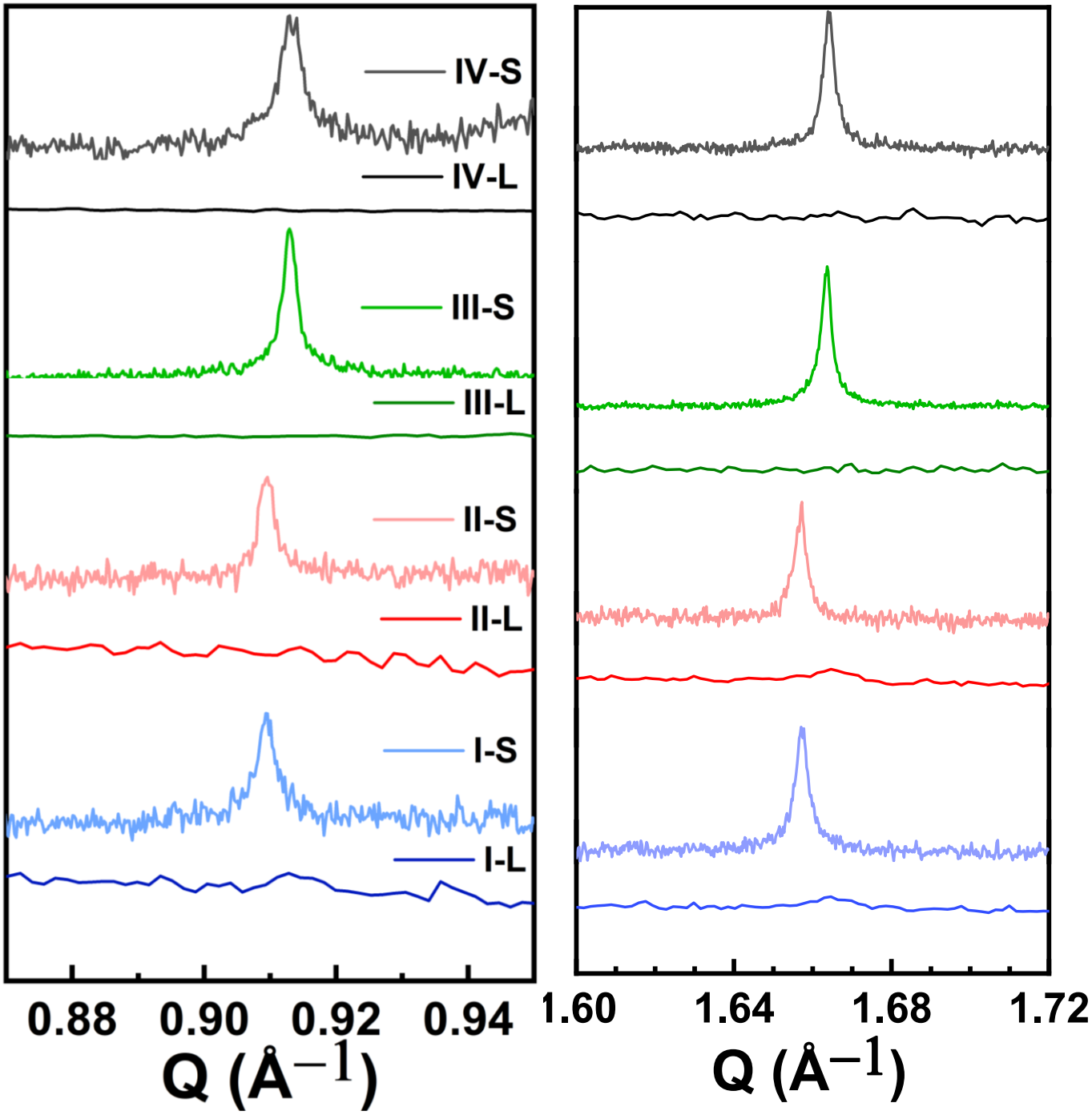

Fig. S4. A close-up view of sections of synchrotron PXRD and lab-PXRD of **I** – **IV**, plotted in terms of Q vectors (Å^{-1}) showing the presence of lines at Q = 0.9135 Å^{-1} (d = 6.884 Å) and Q = 1.662 Å^{-1} (d = 3.779 Å) for (101) and (211) diffraction lines, respectively, only in the synchrotron pattern but flat line in lab-data.

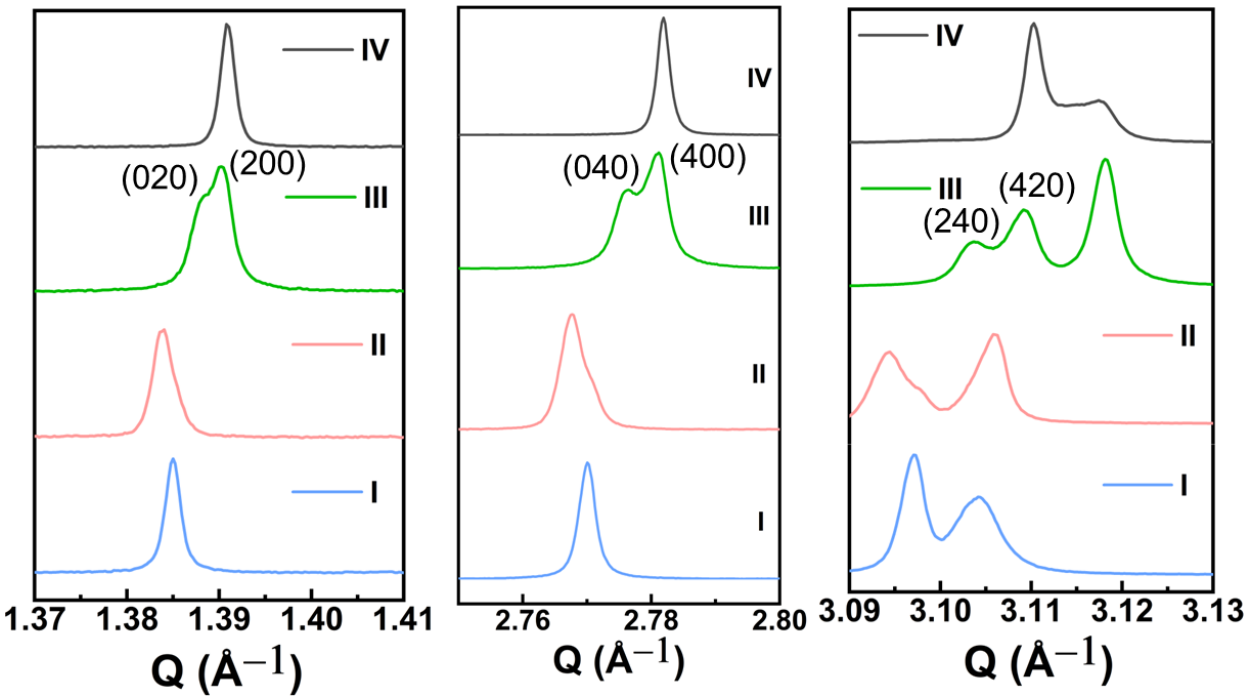

Fig. S5. Sections of the synchrotron PXRD plots showing the distortion in **III** at $d = 4.519$ Å/$Q = 1.3905$ Å^{-1} (200) line, $d = 2.259$ Å/$Q = 2.78$ Å^{-1} (400) line, or $d = 2.0207$ Å/$Q = 3.1093$ Å^{-1} (420) line through the stack plot of **I**-**IV**.

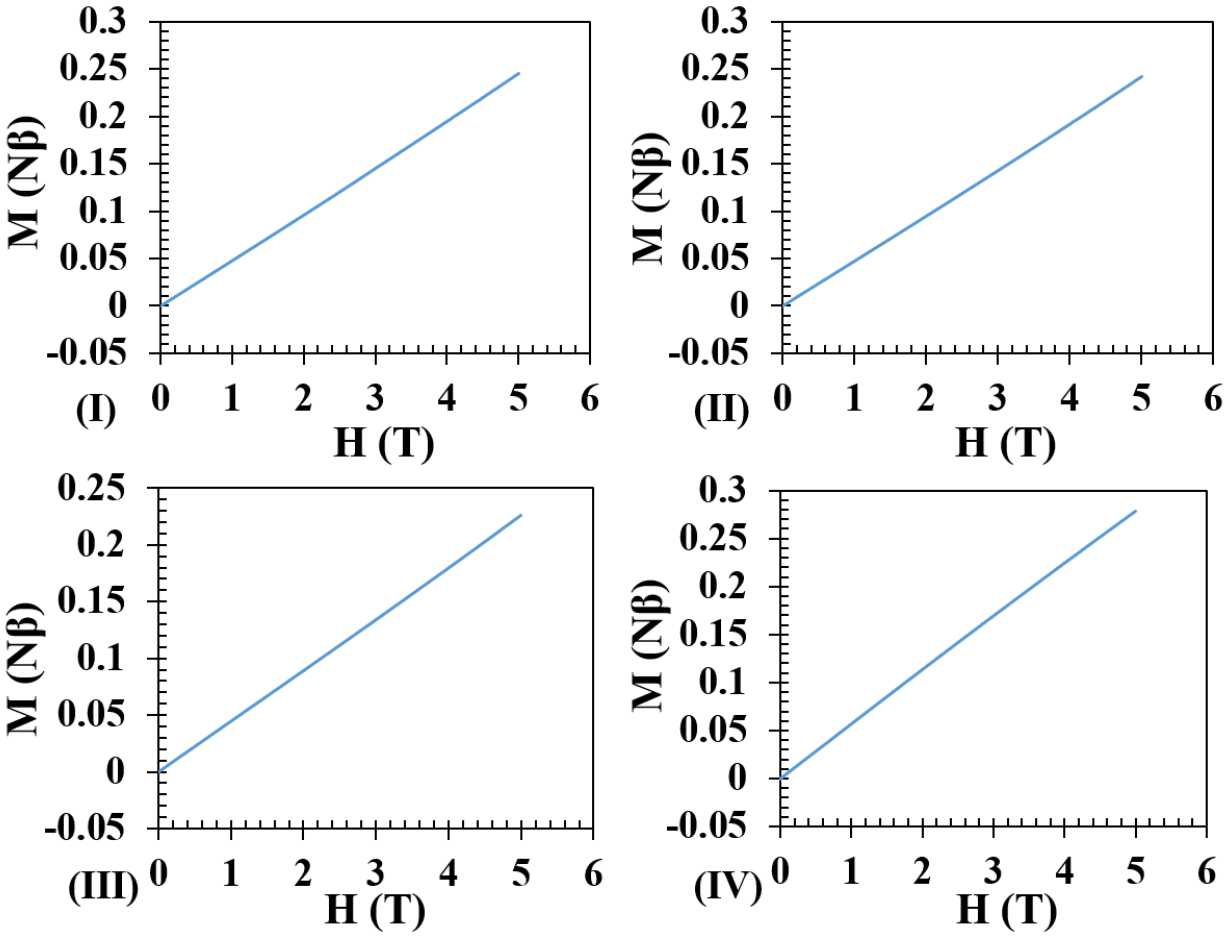

Fig. S6. M vs H plots of four compounds, **I** – **IV**, at 5K.

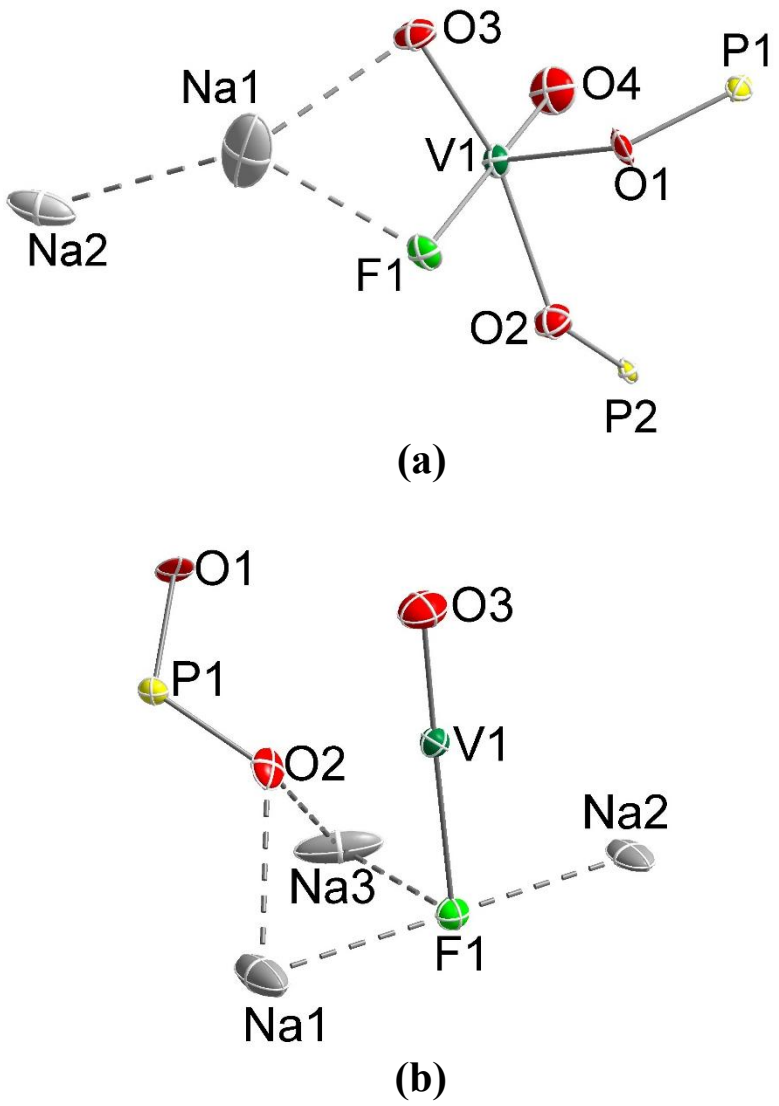

Fig. S7. Asymmetric unit of **I**, **II** and **IV** in $P4_2/mnm$ (a) compared with the asymmetric unit of **III** crystallized in *Amam* space group (b).

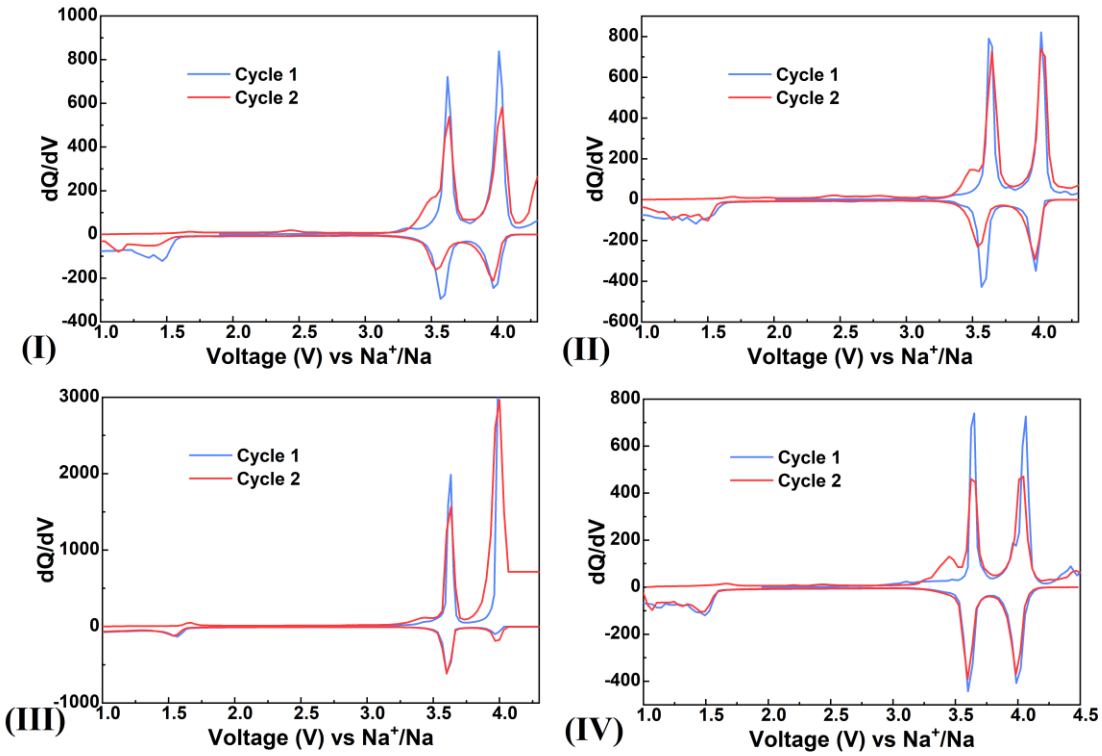

Fig. S8. dQ/dV curves for the first two cycles of charge-discharge at C/50 rate for **I** – **IV** in Na-ion batteries cycled between 1 – 4.5 V.

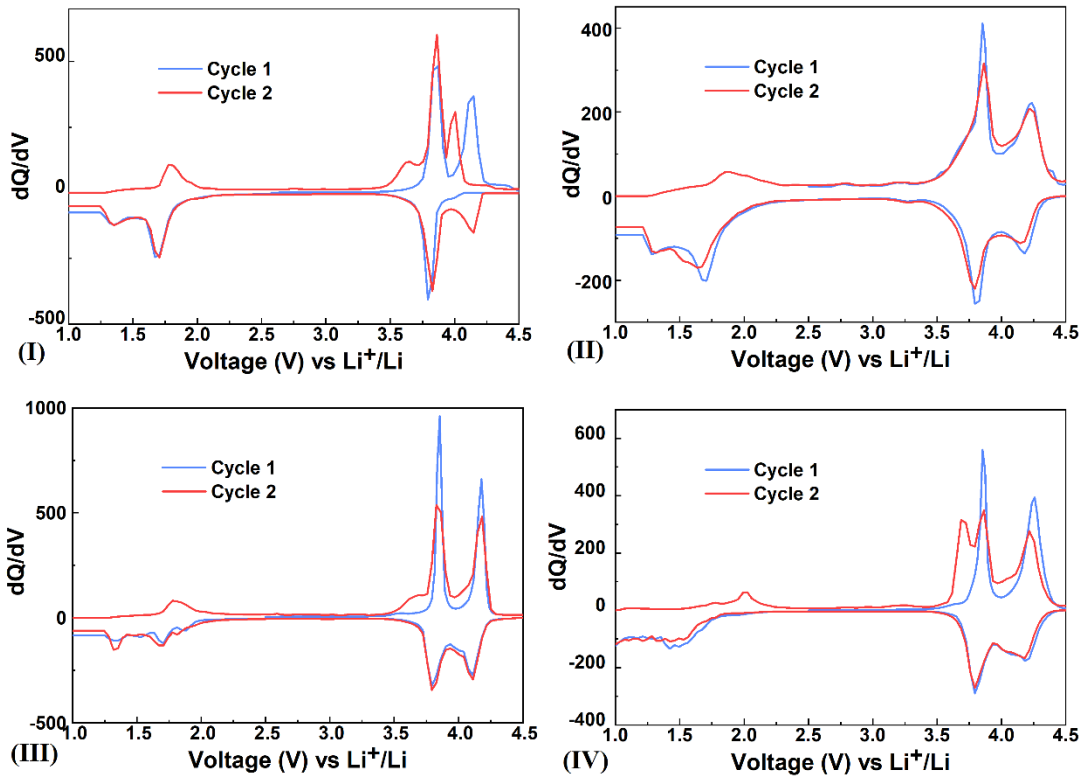

Fig. S9. dQ/dV curves for the first two cycles of charge-discharge at C/50 rate for **I** – **IV** in Li-ion batteries cycled between 1 – 4.5 V.

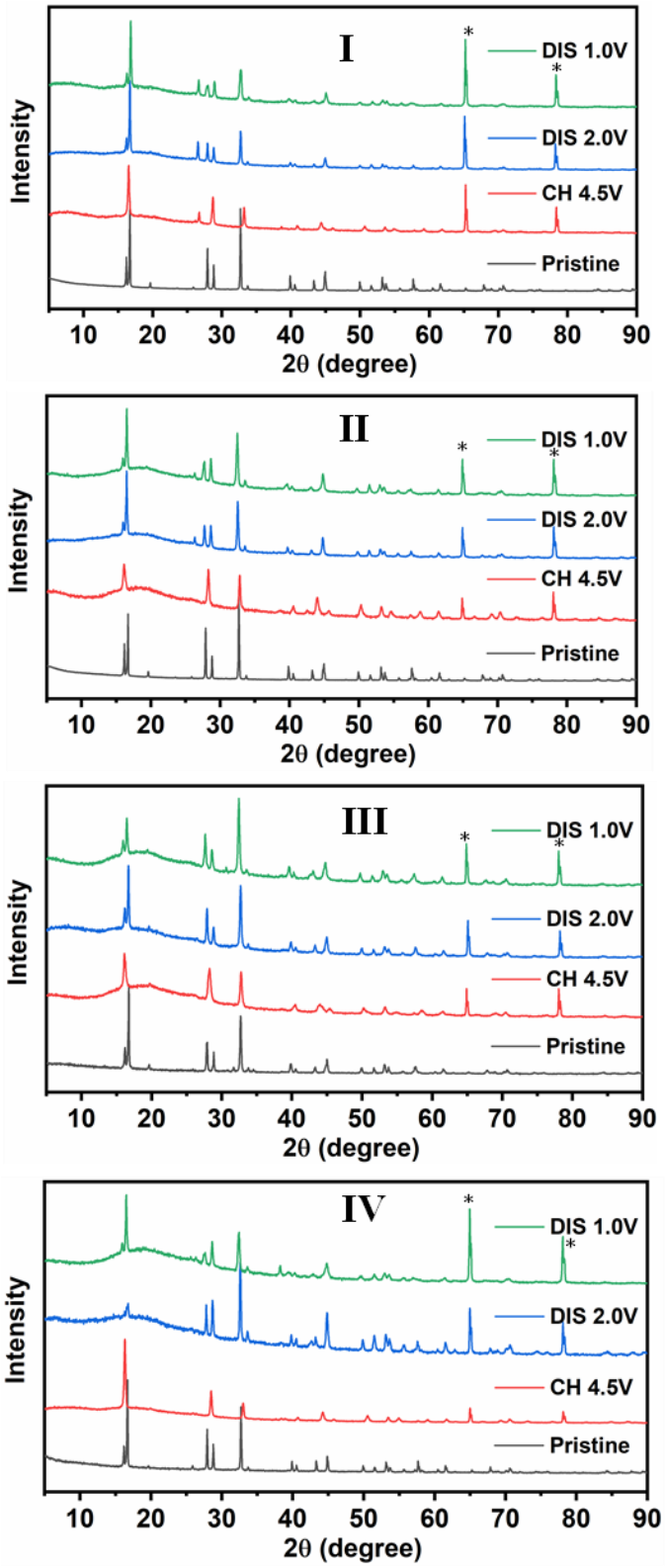

Fig. S10. PXRDs of the cathodes made of compounds, **I** – **IV**, recovered at different state of charge and discharge with respect to Na^+/Na in a Na-ion battery. The asterisks indicate diffraction lines from the Al-current collector.

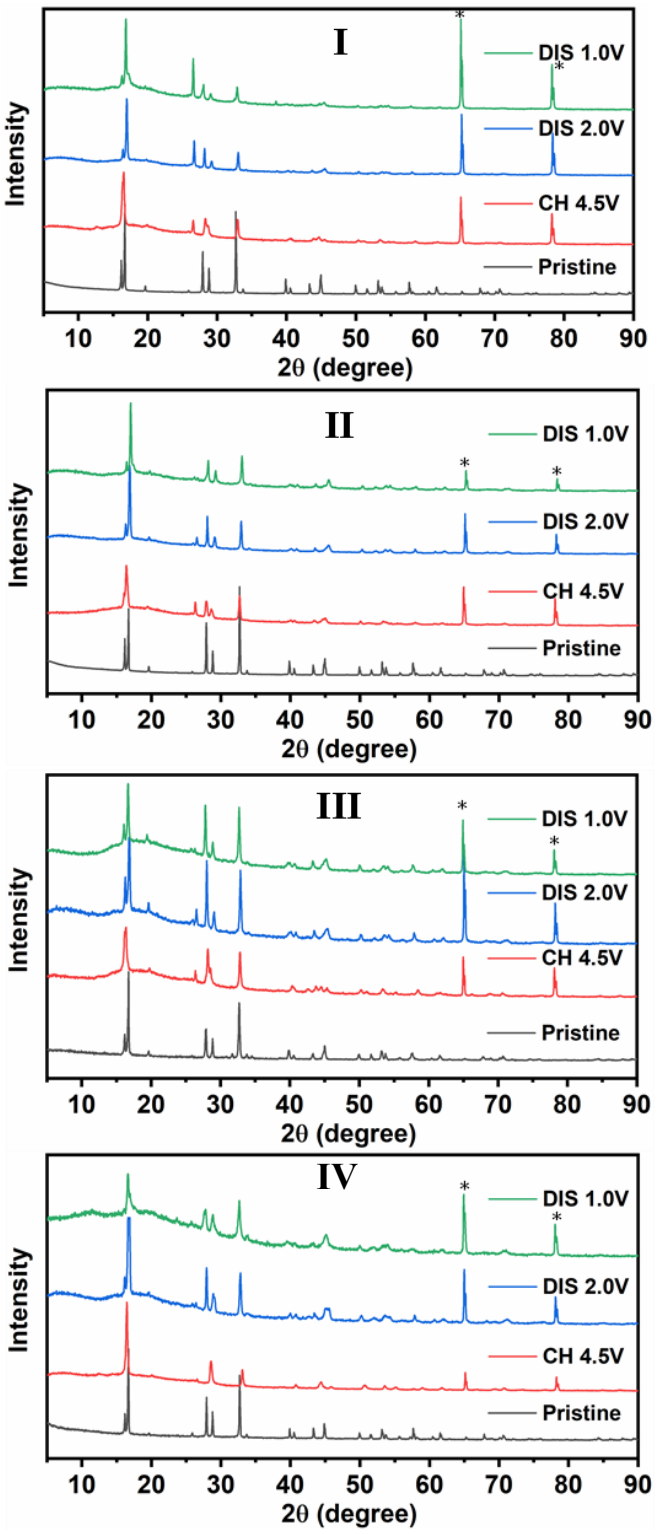

Fig. S11. PXRDs of the cathodes made of compounds, **I** – **IV**, recovered at different state of charge and discharge with respect to Li^+/Li in a Li-ion battery. The asterisks indicate diffraction lines from the Al-current collector.

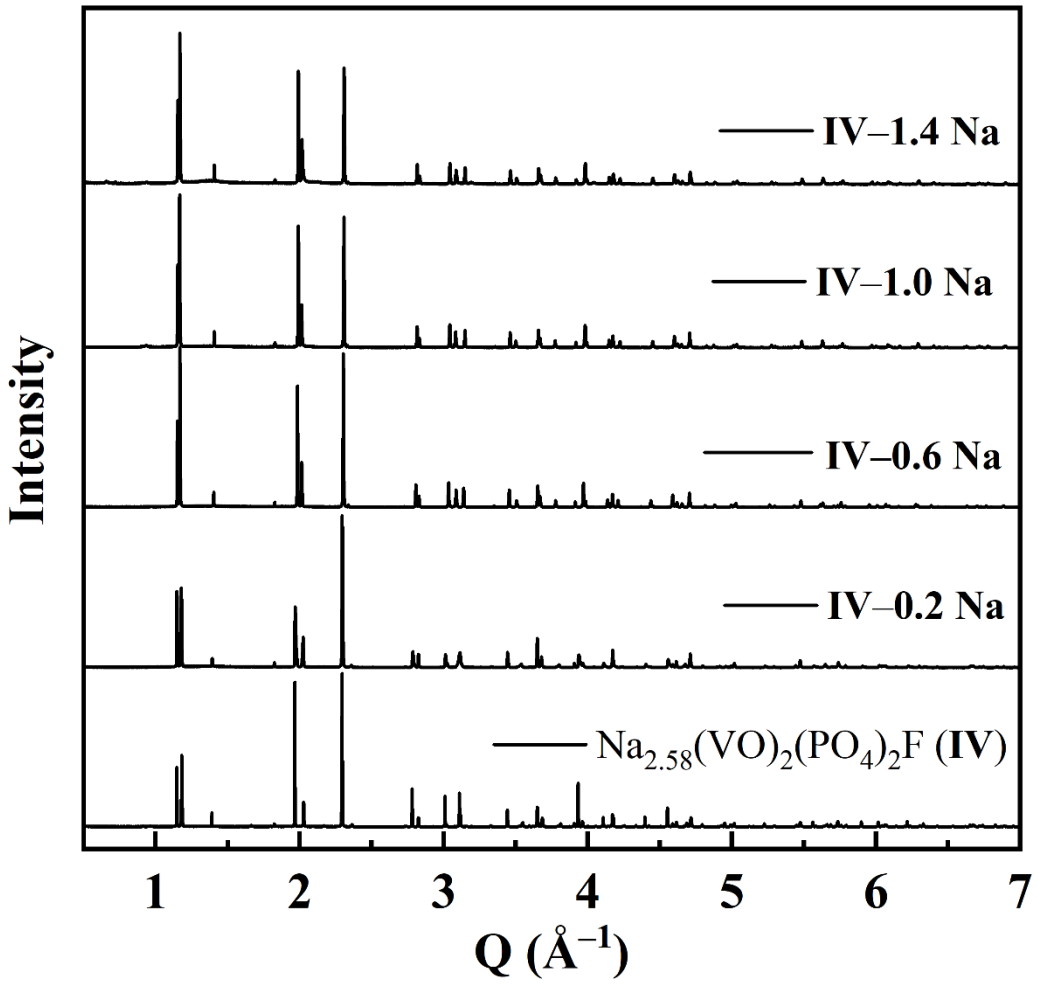

Fig. S12. Synchrotron PXRDs of the pristine compound, **IV** and it's chemically oxidized forms with increasing ratios of oxidizing agent, NO_2BF_4, as described in the main text.

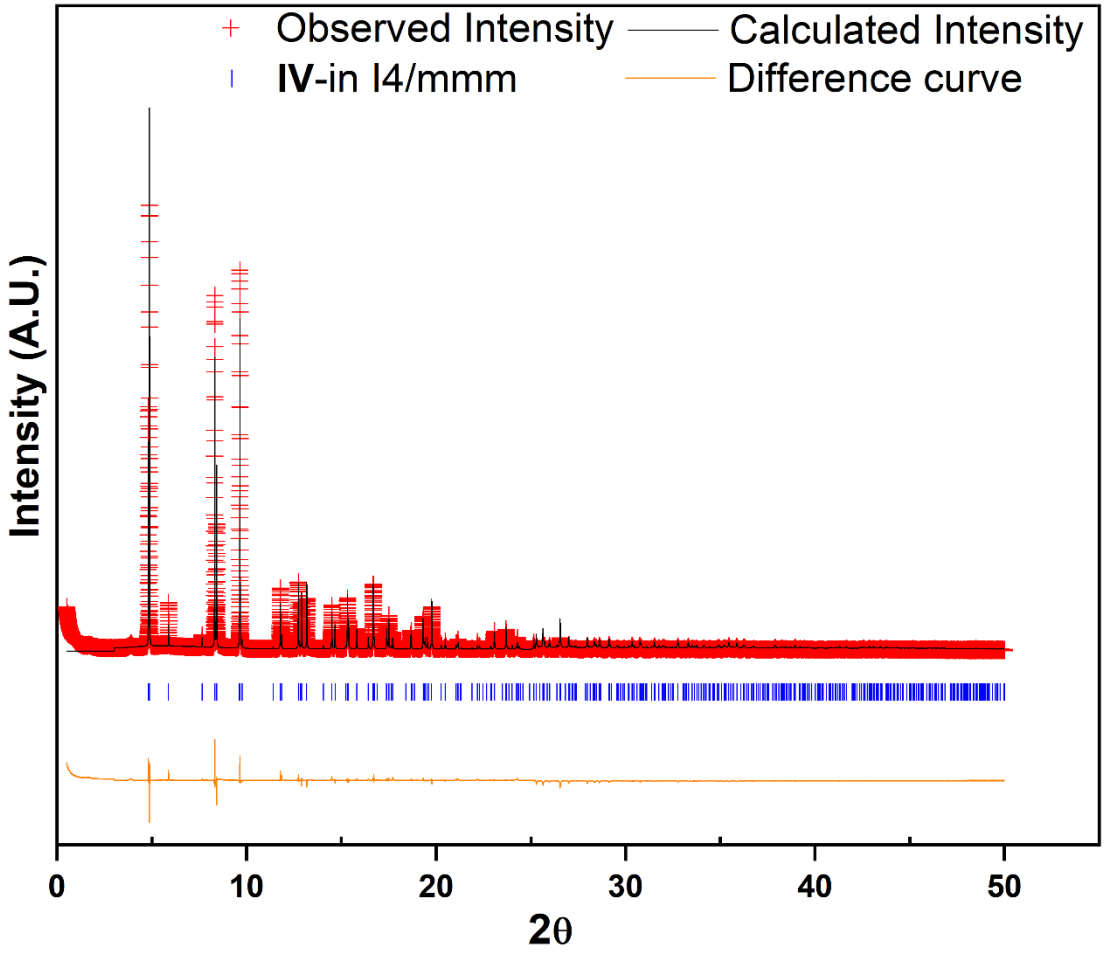

Fig. S13. Rietveld refinement of S-PXRD data of the oxidized sample of **IV,** referred as **IV-1.0** (see main text) showing the observed, calculated, and difference curve along with reflection ticks for the model crystal structure. $\lambda = 0.458092$ Å, $R_f = 0.108$, W_R (Prof) = 0.162.

Table S1. Atomic coordinates and equivalent isotropic displacement parameters (Å2) of **I**.

Atom	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U(eq) [Å²]
V1	8*j*	..m	1.0000	0.25071(10)	0.25071(10)	0.19974(8)	0.010(1)
P1	4*d*	-4..	1.0000	0	1/2	1/4	0.008(1)
P2	4*e*	2.mm	1.0000	0	0	0.2473(2)	0.005(1)
O1	16*k*	1	1.0000	0.0954(5)	0.4040(5)	0.1635(5)	0.013(1)
O2	8*j*	..m	1.0000	0.0961(5)	0.0961(5)	0.1614(6)	0.015(2)
O3	8*j*	..m	1.0000	0.4042(5)	0.4042(5)	0.1654(6)	0.015(2)
F1	4*f*	m.2m	1.0000	0.2510(4)	0.2510(4)	0	0.012(1)
O4	8*j*	..m	1.0000	0.2501(4)	0.2501(4)	0.3542(4)	0.022(1)
Na1	8*i*	m..	0.6848	0.5179(7)	0.2599(13)	0	0.054(2)
Na2	8*i*	m..	0.7912	0.742(1)	0.0134(5)	0	0.033(1)

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å2) of **II**.

Atom	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U(eq) [Å²]
V1	8*j*	..m	1.000	0.25092(6)	0.25092(6)	0.19982(6)	0.009(1)
P1	4*d*	-4..	1.000	0	1/2	1/4	0.007(1)
P2	4*e*	2.mm	1.000	0	0	0.2467(5)	0.006(1)
O1	16*k*	1	1.000	0.0957(3)	0.4042(3)	0.1638(4)	0.014(1)
O2	8*j*	..m	1.000	0.0955(3)	0.0955(3)	0.1606(4)	0.014(1)
O3	8*j*	..m	1.000	0.4041(3)	0.4041(3)	0.1659(5)	0.014(1)
F1	4*f*	m.2m	1.000	0.2515(3)	0.2515(3)	0	0.011(1)
O4	8*j*	..m	1.000	0.2507(3)	0.2507(3)	0.3538(3)	0.020(1)
Na1	8*i*	m..	0.6332	0.5170(5)	0.2671(8)	0	0.047(2)
Na2	8*i*	m..	0.832	0.7397(5)	0.0123(3)	0	0.030(1)

Table S3. Atomic coordinates and equivalent isotropic displacement parameters (Å2) of **III**.

Atom	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U(eq) [Å²]
V1	8*g*	..m	1.00	1/4	0.2498(3)	0.19969(10)	0.009(1)
P1	8*e*	2..	1.00	0	0	0.2501(4)	0.007(1)
F1	4*c*	m2m	1.00	1/4	0.2517(10)	0	0.011(1)
O1	16*h*	1	1.00	0.0946(5)	0.4036(5)	0.1629(5)	0.013(1)
O2	16*h*	1	1.00	0.0973(6)	0.0959(6)	0.1636(5)	0.014(1)
O3	8*g*	..m	1.00	1/4	0.2511(10)	0.3531(4)	0.021(1)
Na1	4*c*	m2m	0.8	1/4	-0.0218(10)	0	0.042(3)
Na2	4*c*	m2m	0.68	1/4	0.5069(10)	0	0.030(3)
Na3	8*f*	m..	0.76	-0.0151(5)	0.2441(12)	0	0.040(1)

Table S4. Atomic coordinates and equivalent isotropic displacement parameters (Å2) of **IV**.

Atom	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U(eq) [Å²]
V1	8*j*	..m		0.25053(6)	0.25053(6)	0.19709(7)	0.009(1)
P1	4*d*	-4..		0	1/2	1/4	0.005(1)
P2	4*e*	2.mm		0	0	0.24895(15)	0.005(1)
O1	16*k*	1		0.0960(3)	0.4043(3)	0.1641(2)	0.012(1)
O2	8*j*	..m		0.0959(2)	0.0959(2)	0.1635(3)	0.014(1)
O3	8*j*	..m		0.4043(3)	0.4043(3)	0.1652(3)	0.015(1)
F1	4*f*	m.2m		0.2507(3)	0.2507(3)	0	0.011(1)
O4	8*j*	..m		0.2506(3)	0.2506(3)	0.3533(4)	0.022(1)
Na1	8*i*	m..	0.646	0.5221(5)	0.2554(5)	0	0.042(1)
Na2	8*i*	m..	0.646	0.7487(5)	0.0204(5)	0	0.036(1)

Table S5. Selected interatomic distances of **I** – **IV** from single-crystal structure solutions.

*P*4$_2$/*mnm*	**I**	**II**	**IV**	*Amam*	**III**
V 1 – O4	1.642(4)	1.636(3)	1.666(5)	V1 – O3	1.620(5)
V1 – O3	1.998(6)	1.992(4)	1.994(4)	2 x V1 – O2$^{\#1}$	1.993(5)
2 x V1 – O1$^{\#1}$	2.012(5)	2.010(3)	2.002(2)	2 x V1 – O1$^{\#1}$	2.011(5)
V1 – O2	2.019(6)	2.031(4)	2.009(3)	V1 – F1	2.109(3)
V1 – F1	2.1232(8)	2.1224(7)	2.1022(8)	**BVS sum**	**4.1185**
BVS sum	**3.9668**	**3.989**	**3.9433**	2 x P1 – O1$^{\#2, \#3}$	1.526(6)
4 x P1 – O1$^{\#5, \#6, \#7}$	1.531(5)	1.529(4)	1.529(2)	2 x P1 – O2$^{\#4}$	1.535(6)
2 x P2 – O2$^{\#9}$	1.532(7)	1.526(4)	1.528(3)	4 x Na1 – O2	2.452(7)
2 x P2 – O3$^{\#7, \#10}$	1.536(7)	1.539(4)	1.529(3)	2 x Na1 – O3$^{\#5}$	2.570(6)
2 x Na1 – O1$^{\#4}$	2.509(9)	2.543(6)	2.505(4)	Na1 – F1	2.470(5)
2 x Na1 – O3$^{\#4}$	2.419(9)	2.384(5)	2.460(4)	4 x Na2 – O1	2.408(6)
2 x Na1 – O4$^{\#8, \#11}$	2.612(6)	2.627(5)	2.592(5)	2 x Na2 – O3$^{\#7}$	2.696(9)
Na1 – F1	2.416(7)	2.406(5)	2.453(6)	Na2 – F1	2.304(13)
2 x Na2 – O1$^{\#2}$	2.394(7)	2.383(4)	2.467(4)	2 x Na3 – O1	2.452(9)
2 x Na2 – O2$^{\#2, \#3}$	2.463(8)	2.466(4)	2.474(4)	2 x Na3 – O2	2.409(8)
2 x Na2 – O4$^{\#8, \#11}$	2.642(5)	2.649(4)	2.595(5)	2 x Na3 – O3$^{\#3, \#6}$	2.628(5)
Na2 – F1$^{\#2}$	2.392(5)	2.387(4)	2.451(5)	Na3 – F1	2.393(5)

Symmetry transformations used to generate equivalent atoms:

For **I**, **II**, and **IV:**

#1 y, x, z; #2 -y, -x+1, z; #3 -x+1, -y, -z; #4 y, x, -z; #5 -y+1/2, x+1/2, -z+1/2; #6 -x, -y+1, z; #7 y-1/2, -x+1/2, -z+1/2; #8 x-1/2, -y+1/2, z+1/2; #9 -x, -y, z; #10 -y+1/2, x-1/2, -z+1/2; #11 -y+1/2, x-1/2, z+1/2.

For **III**: #1 -x+1/2, y, z; #2 x, y-1/2, -z+1/2; #3 -x, -y+1/2, -z+1/2; #4 -x, -y, z; #5 x, y+1/2, z+1/2; #6 x+1/2, -y+1/2, -z+1/2; #7 x, y-1/2, z+1/2.

Table S6. Refined lattice constants and final Rietveld refinement parameters from the synchrotron powder XRD for the four compounds.

Compounds	I	II	III	IV
Empirical formula	$Na_{2.922}(VO)_2(PO_4)_2F$	$Na_{2.939}(VO)_2(PO_4)_2F$	$Na_{2.97}(VO)_2(PO_4)_2F$	$Na_{2.646}(VO)_2(PO_4)_2F$
Formula weight	410.60	410.4	411.09	403.66
Temperature(K)	295	295	300	300
Wavelength (Å)	0.45790	0.45787	0.45973	0.41283
Crystal system	Tetragonal	Tetragonal	Orthorhombic	Tetragonal
Space group	$P4_2/mnm$	$P4_2/mnm$	*Amam*	$P4_2/mnm$
***a*/Å**	9.039058(12)	9.043427	9.03613(4)	9.03466
b/Å	9.039058(12)	9.043427	9.04909(5)	9.03466
c/Å	10.623426(18)	10.616009	10.61623(3)	10.62553
Volume/ $Å^3$	867.9824(30)	868.215	868.075(6)	867.312
Z	4	4	4	4
Density (calculated)	3.1374 Mg/m^3	3.1397 Mg/m^3	3.1455 Mg/m^3	3.0913 Mg/m^3
Number of reflections	1578	1580	1537	2135
R_f^2 (%)	0.05659	0.06933	0.09062	0.0734
R_w (%)	0.09577	0.13301	0.16401	0.13974
V = O Å	1.620	1.618	1.611	1.632

Table S7. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) of **I**.

Atom	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U(eq) [$Å^2$]
V1	8j	..m	1.00	0.25014	0.25014	0.19937	0.0093
P1	4d	-4..	1.00	0	1/2	1/4	0.0087
P2	4e	2.mm	1.00	0	0	0.24654	0.0034
O1	16k	1	1.00	0.09421	0.40548	0.16299	0.0069
O2	8j	..m	1.00	0.09605	0.09605	0.16286	0.0132
O3	8j	..m	1.00	0.40353	0.40353	1/6	0.0091
F1	4f	m.2m	1.00	0.25250	0.25250	0	0.0084
O4	8j	..m	1.00	0.25059	0.25059	0.35163	0.0173
Na1	8i	m..	0.6462	0.52176	0.27867	0	0.0201
Na2	8i	m..	0.8145	0.74448	0.01253	0	0.0428

Table S8. Atomic coordinates and equivalent isotropic displacement parameters (Å2) of **II**.

Atom	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U(eq) [Å²]
V1	8j	..m	1.00	0.25049	0.25049	0.19958	0.0092
P1	4d	-4..	1.00	0	1/2	1/4	0.0098
P2	4e	2.mm	1.00	0	0	0.24619	0.0031
O1	16k	1	1.00	0.09484	0.40586	0.16369	0.0088
O2	8j	..m	1.00	0.09729	0.09729	0.16543	0.0062
O3	8j	..m	1.00	0.40354	0.40354	0.16409	0.0155
F1	4f	m.2m	1.00	0.25181	0.25181	0	0.0088
O4	8j	..m	1.00	0.25051	0.25051	0.35201	0.0200
Na1	8i	m..	0.636	0.52262	0.27842	0	0.0119
Na2	8i	m..	0.8336	0.74699	0.01080	0	0.0446

Table S9. Atomic coordinates and equivalent isotropic displacement parameters (Å2) of **III**.

Atom	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U(eq) [Å²]
V1	8*g*	..m	1.00	0.25000	0.24763	0.19959	0.0088
P1	8*e*	2..	1.00	0.00000	0.00000	0.25584	0.0063
F1	4*c*	m2m	1.00	0.25000	0.24306	0.00000	0.0097
O1	16*h*	1	1.00	0.09029	0.40793	0.16114	0.0112
O2	16*h*	1	1.00	0.10052	0.09785	0.16596	0.0094
O3	8*g*	..m	1.00	0.25000	0.26302	0.35081	0.0143
Na1	4*c*	m2m	0.8162	0.25000	-0.01565	0.00000	0.0689
Na2	4*c*	m2m	0.6648	0.25000	0.51652	0.00000	0.0268
Na3	8*f*	m..	0.7442	-0.01607	0.23120	0.00000	0.0337

Table S10. Atomic coordinates and equivalent isotropic displacement parameters (Å2) of **IV**.

Atom	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U(eq) [Å^2]
V1	8j	..m	1.00	0.25069	0.25069	0.19879	0.0092
P1	4d	-4..	1.00	0	1/2	1/4	0.0065
P2	4e	2.mm	1.00	0	0	0.24143	0.0040
O1	16k	1	1.00	0.09401	0.40421	0.16289	0.0092
O2	8j	..m	1.00	0.09347	0.09347	0.16361	0.0120
O3	8j	..m	1.00	0.40263	0.40263	0.16481	0.0107
F1	4f	m.2m	1.00	0.25810	0.25810	0	0.0063
O4	8j	..m	1.00	0.23884	0.23884	0.35119	0.0115
Na1	8i	m..	0.6883	0.51912	0.27051	0	0.0261
Na2	8i	m..	0.6348	0.74883	0.02053	0	0.0316

Table S11. Inter-atomic distances of **I** – **IV** generated from the Rietveld refinement.

$P4_2/mnm$	**I**	**II**	**IV**	*Amam*	**III**
V 1 – O4	1.621(4)	1.618(3)	1.632(5)	V1 – O3	1.611(3)
V1 – O3	1.992(4)	1.993(6)	1.974(4)	2 x V1 – O2	1.946(4)
2 x V1 – O	2.026(4)	2.025(2)	2.0182(4)	2 x V1 – O1	2.086(6)
V1 – O2	2.007(7)	1.993(4)	2.009(3)	V1 – F1	2.119(4)
V1 – F1	2.118(6)	2.118(6)	2.1144(8)	2 x P1 – O1	1.462(4)
4 x P1 – O1	1.519(4)	1.516(5)	1.525(2)	2 x P1 – O2	1.587(7)
2 x P2 – O2	1.516(8)	1.511(4)	1.4526(5)	4 x Na1 – O2	2.446(6)
2 x P2 – O3	1.542(6)	1.558(4)	1.5938(7)	2 x Na1 – O3	2.553(2)
2 x Na1 – O1	2.623(8)	2.625(5)	2.572(3)	Na1 – F1	2.341(5)
2 x Na1 – O3	2.353(8)	2.339(7)	2.366(3)	4 x Na2 – O1	2.444(6)
2 x Na1 – O4	2.614(7)	2.605(6)	2.539(6)	2 x Na2 – O3	2.735(9)
Na1 – F1	2.445(6)	2.460(5)	2.361(5)	Na2 – F1	2.474(3)
2 x Na2 – O1	2.401(6)	2.417(6)	2.445(2)	2 x Na3 – O1	2.531(8)
2 x Na2 – O2	2.456(7)	2.454(5)	2.472(3)	2 x Na3 – O2	2.381(7)
2 x Na2 – O4	2.659(6)	2.669(4)	2.689(6)	2 x Na3 – O3	2.642(4)
Na2 – F1	2.395(5)	2.375(4)	2.518(4)	Na3 – F1	2.406(6)

Table S12. Inter-sodium distances in **I** – **IV** obtained from single-crystal structure solution.

	I	**II**	**IV**		**III**
Na1 – Na1$^{\#2}$	2.84(2)	2.76(3)	2.84(3)	2 x Na1 – Na3$^{\#4, \#5}$	2.92(2)
Na1 – Na2	3.01(3)	3.06(4)	2.95(2)	Na1 – Na3$^{\#3}$	3.39(3)
Na1 – Na1$^{\#1}$	3.30(3)	3.20(2)	3.41(3)	2 x Na2 – Na3$^{\#6, \#7}$	3.09(3)
Na2 – Na2$^{\#2}$	3.13(3)	3.17(2)	2.95(3)	Na2 – Na3$^{\#3}$	3.37(2)

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ y, x, -z; $^{\#2}$ -y + 1, -x + 1, z; $^{\#3}$ -x + 1/2, y, z; $^{\#4}$ -x, -y, -z; $^{\#5}$ x + 1/2, -y, -z; $^{\#6}$ x + 1/2, -y+1, -z; $^{\#7}$ -x, -y + 1, -z.

Table S13. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of **IV-1.0**.

Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å^2]**
V1	4*e*	4mm	1.0	0	0	0.19348	0.0195
P1	4*d*	-4m2	1.0	0	1/2	1/4	0.0085
O1	16*n*	.m.	1.0	0	0.3146	0.1633	0.0185
O2	4*e*	4mm	1.0	0	0	0.3395	0.0156
F1	2*a*	4/mmm	1.0	0	0	0	0.0196
Na1	8*h*	m.2m	0.60(2)	0.27113	0.27113	0	0.0503